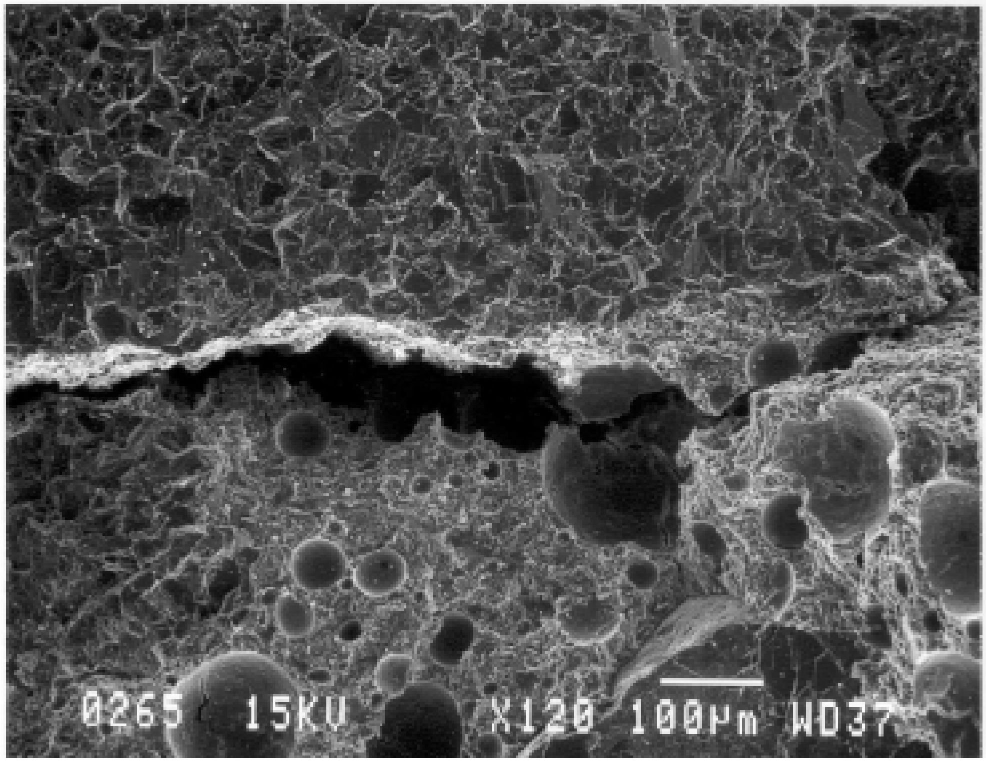
South Dakota
Department of Transportation
Office of Research

U.S. Department
of Transportation
Federal Highway
Administration

SD1998-03-F



Investigation of Low Compressive Strengths of Concrete in Paving, Precast and Structural Concrete

Study SD1998-03

Final Report

South Dakota Department of Transportation
Office of Research
700 East Broadway Avenue
Pierre, SD 57501-2586

August, 2000

DISCLAIMER

ACKNOWLEDGEMENTS

This work was performed under the supervision of the SD98-03 Technical Panel:

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The researchers would like to express appreciation to Dacotah Cement, Rapid City, SD for financial support and Don Campbell of Campbell Petrographic Services, Dodgeville, WI for the petrographic analyses of cement and concrete samples. The work was performed in cooperation with the United States Department of Transportation Federal Highway Administration.

TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. SD98-03-F	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Investigation of Low Compressive Strengths of Concrete Paving, Precast and Structural Concrete		5. Report Date August, 2000	
		6. Performing Organization Code	
7. Author(s) William Cross, Edward Duke, Jon Kellar, Dan Johnston		8. Performing Organization Report No.	
9. Performing Organization Name and Address South Dakota Department of Transportation; SDSM&T Office of Research ; College of Material Sciences 700 East Broadway Avenue;501 E. St. Joseph St. Pierre, SD 57501-2586 ;Rapid City, SD 57701-3995		10. Work Unit No.	
		11. Contract or Grant No. 310581	
12. Sponsoring Agency Name and Address South Dakota Department of Transportation Office of Research 700 East Broadway Avenue Pierre, SD 57501-2586		13. Type of Report and Period Covered Final; February, 1998 to October, 1999	
		14. Sponsoring Agency Code	

15. Supplementary Notes
An executive summary of this report is published as SD98-03-X.

16. Abstract

This research examines the causes for a high incidence of catastrophically low compressive strengths, primarily on structural concrete, during the 1997 construction season. The source for the low strengths was poor aggregate-paste bond associated with air void clusters and poorly formed cement paste in the interfacial region adjacent to the aggregate. An interaction between the “synthetic” air entraining admixtures, used as substitutes for vinsol resin, and low alkali cements was directly tied the problem with high summertime temperatures also contributing to the problem. The “synthetics” appear to be more hydrophobic, form thinner-walled air bubbles and develop rapid draining bubble flocculations more readily than vinsol resin, all of which can lead to significant reductions in strength. As an interim measure, the Department specified the sole use of vinsol resin air entraining agents along with water reducers, as needed, in April, 1998 and these measures have minimized the incidence of low strengths.Petrographic analysis of cores taken from low strength concretes failed to reveal the causes of the low strength problem but SEM microscopy clearly showed the failure mechanism. Laboratory testing of concrete mixes with various air entraining admixtures demonstrated an interaction was taking place with one cement and petrographic and chemical analysis of the cements used in the testing implicated alkali sulfates as a potential source of the interaction. Testing of the “synthetic” air entraining admixtures showed they have substantially different properties compared to vinsol resins. Mixtures of the “synthetics” and vinsol resin with 50 % or more vinsol resin behaved similarly to vinsol alone.

17. Keyword concrete admixtures, air entraining agents, low compressive strengths		18. Distribution Statement No restrictions. This document is available to the public from the sponsoring agency.	
19. Security Classification (of this report) Unclassified	Security Classification (of this page) Unclassified	21. No. of Pages	22. Price

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Problem Description

Introduction

During the 1997 construction season the South Dakota Department of Transportation (SDDOT) experienced an unacceptably high number of failing concrete cylinder compressive strength tests. As the season progressed the incidence of failure increased statewide. On October 9, 1997 a problem solving meeting to discuss these low strengths was held in Pierre with SDDOT personnel, contractors, aggregate producers, cement manufacturers, concrete admixture producers and redi-mix concrete plant operators in attendance. The purpose of the meeting was to determine if there was a cause or causes which could explain the low strengths and any appropriate steps taken to eliminate the problem. A preliminary analysis of the failures produced the following:

1) Four different brands of Portland cement were used in failing concrete.
2) Concrete containing granite, limestone and quartzite coarse aggregate failed.
3) Failures were statewide.
4) Most failing cylinders had normal air, slump and unit weights.
5) Compressive strengths on cores taken of failing concrete tended to correlate with cylinders.
6) Failures generally occurred during the summer months.
7) Use of a water reducer substantially reduced the incidence of failing strengths.

Amongst the possible causes for the low compressive strengths listed at this meeting were

1) cement
2) dirty rock
3) mix design too harsh
4) air entraining admixtures
5) high water-cement ratios
6) high air contents
7) temperature
8) concrete mixing time

The methods by which the possible causes were investigated are given in the Findings section in the purpose of the tests. Although the problem solving meeting did not generate a solution, the group unanimously agreed that research was necessary and the Department assigned it a high priority to prevent a recurrence next year.

Background

In an initial attempt to obtain any indications of what could be causing problems with the development of specified 28 day compressive strengths, several randomly selected 6" x 12" cylinders with both limestone and quartzite coarse aggregate were taken to the South Dakota School of Mines and Technology (SDSM&T) for scanning electron microscopy (SEM) examination. Aggregate pieces were removed from the concrete matrix and the surface of the aggregate and its corresponding cement paste matrix were scanned to determine if there was a problem at the interface between the two. Both aggregates exhibited clusters of flocculated air bubbles on their surfaces which were mirrored exactly in the paste. Figures 1 and 2 illustrate the anomalous air voids and indicate that failure occurred via shear through the void clusters which could possibly explain the low strengths.

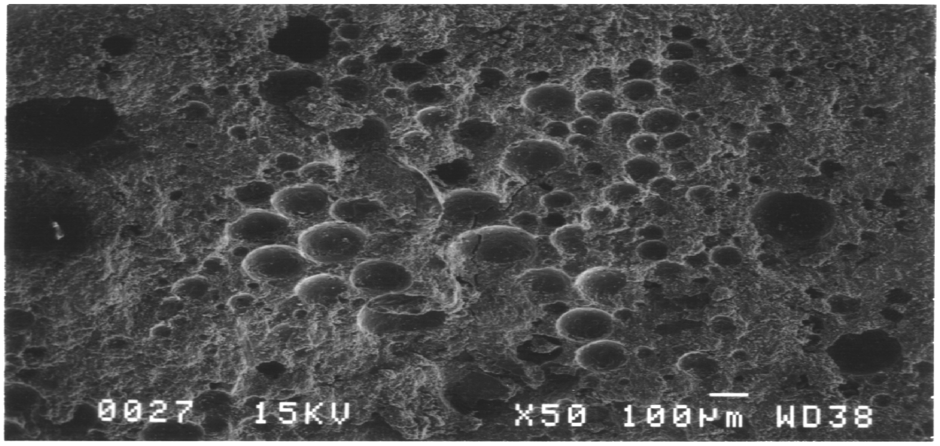


Figure 1. Limestone paste surface at 50 x as found by SEM.

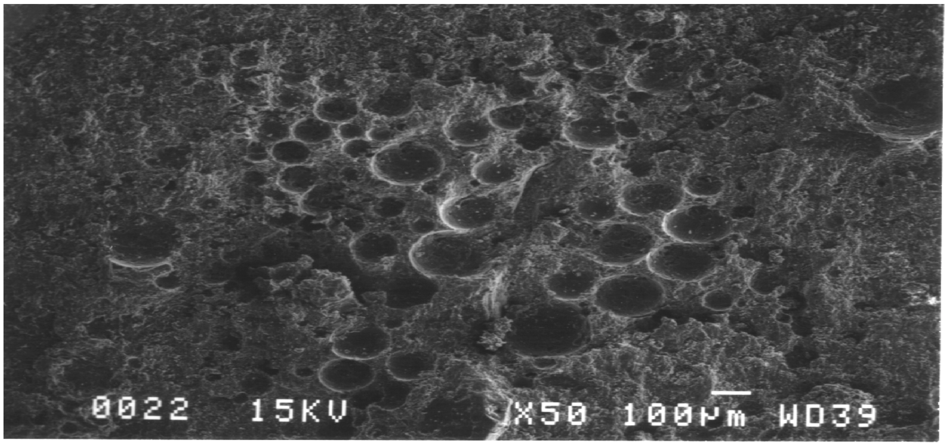


Figure 2. Limestone aggregate surface at 50 x as found by SEM.

General Discussion of Compressive Strength Failures

Failing compressive strength tests on cylinders are not uncommon during a typical construction season. The usual reasons for such failures are too high a water-cement ratio, too high an air content, cement, improper mixing and handling of the concrete and improper fabrication and handling of the cylinders. Normally, low strength concrete causes delays during construction but additional testing of cores at ages later than 28 days indicate that the concrete has achieved design strength. The primary difference between prior strength failures and those which occurred during the 1997 construction season was the occasional lack of any tendency for compressive strength to increase with time. A significant number of structural elements which had low compressive strength test results at 28 days did not increase in strength with time.

Cylinder and core specimens taken to failure exhibited a characteristic lack of aggregate fracture and numerous shearing failures at the aggregate-paste bond. In several extremely low compressive strength cylinder specimens (< 3600 psi) the failure resulted in the shearing of the specimen into two halves directly through the longitudinal axis of the cylinder with no evidence of aggregate fracture, whatsoever. All cylinders exhibiting compressive strengths < 4000 psi had characteristic casts of aggregate faces imprinted over much of the fracture surface as shown in Figure 3. The positive aggregate faces generating the casts had little cement paste adhering to their surfaces. These observations implicated the interfacial zone between the aggregate and the paste as the source of the extremely low compressive strengths.

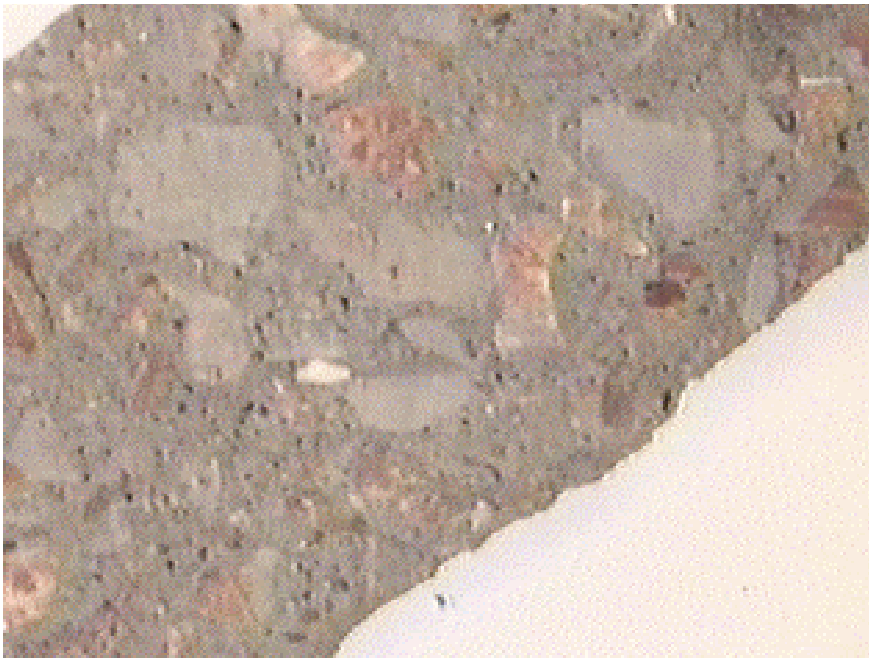


Figure 3. Typical aggregate casts.

Objectives

The research was conducted as a cooperative effort between SDDOT, SDSM&T and Campbell Petrographic Services. The research involved 5 interrelated efforts:

1) literature search and survey of other states and redi-mix concrete plants,
2) petrographic and SEM examination of low strength and normal cores from 1997 projects and laboratory cylinders,
3) laboratory concrete mixes,
4) physical and chemical testing of air-entraining admixtures,
5) project data collection and statistical analysis.

Preliminary information indicated that low strength concrete problems have occurred in several states and have been associated with air entraining admixtures.

The results of this research effort should clearly delineate whether interaction effects of the new air-entraining admixtures with the ingredients used in typical SDDOT concrete mixes is causing a synergistic loss of compressive strength under appropriate conditions. The research also examined other possible causes such as cement content, aggregate gradation and “dirty” aggregate to determine their contributions to the problem.

Task Description

Task 1: Literature Search

Task: The work group at SDSM&T had primary responsibility for the search of available literature on low compressive strength of concrete. This search was a computer based search using the resources of the SDSM&T library. Once the references were identified they were retrieved locally, or through interlibrary loan. SDDOT supplied the necessary available reference documents on the research topic.

Accomplished: The Colorado Association of Research Libraries (CARL) database, amazon.com and several conference proceedings were searched for references concerning causes of low-compressive strength problems and for other materials relevant to this work. A summary of the most important papers is given in the Findings section.

Task 2: Cooperatively Develop Work Plan

Task: The work plan is based primarily upon the meeting of involved project members from SDDOT and SDSM&T held December 15 and 16, 1997 at the SDSM&T campus.

Accomplished: Following the meeting, phone calls and emails were used to finalize the work plan developed December 15 and 16, 1997 in January 1998.

Task 3: Meet with the Technical Panel

Task: Mr. Dan Johnston of SDDOT and the SDSM&T researchers met with the technical panel to discuss the research in Pierre, SD.

Accomplished: The technical pane met at SDSM&T in April 1998 with Mr. Johnston and Drs. Duke and Cross presenting the experimental work plan developed in Task 2.

Task 4: Perform Survey of State DOT's Ready-Mix Plants

Task: The technical panel was primarily responsible for this task. SDSM&T was not involved in preparation of the survey.

Accomplished: This task was not accomplished during the course of the research.

Task 5: Study Database of SDDOT Projects

Task: SDDOT was primarily responsible for this task. SDSM&T was not be involved in this task.

Accomplished: This task was accomplished during the course of the grant.

Task 6: Revise and Submit Testing Plan

Task: A variety of surface chemical tests were performed to evaluate the cause and effects of air bubbles in concrete. These surface chemical tests include, but are not limited to, Fourier transform infrared (FT-IR) spectroscopic examination, surface tension measurements, contact angle goniometry and turbidimetry. In addition, microhardness testing was evaluated as a means to determine low compressive strength concrete.

SDSM&T was responsible for scanning electron microscope (SEM) examination of concrete field cores supplied by SDDOT. Additional laboratory specimens consisting of mortar, concrete, or aggregate were also examined by SEM pending results of laboratory testing of such samples by SDDOT. The purpose of these tests was to compare the microscopic structure of specimens demonstrating low-strength and high-strength performance characteristics.

SDSM&T was responsible for characterizing selected field and/or laboratory specimens by X-ray diffraction (XRD). The purpose of these tests was to examine possible differences in the compounds comprising the cement mortar of specimens demonstrating low-strength and high-strength performance characteristics.

Accomplished: Following Task 3, a revised testing plan was constructed. The revised testing plan is summarized in the Task descriptions of Task 8.

Task 7: Acquire Samples of Vinsol Resin, Cores, and other Mix Components

Task: SDDOT was responsible for the acquisition of the sample components. SDSM&T researchers were responsible for later analyses of the components as defined in Task #8.

Accomplished: Samples were delivered to SDSM&T for testing between April and September, 1998.

Task 8: Complete Laboratory Testing

Task: Surface chemical testing was performed including: qualitative FT-IR examination of the various air entraining admixtures including vinsol resin, Plastocrete 169 and Darex 2. Contact angle measurements were performed using glass slides, polished quartzite and calcite pieces. The aqueous solutions utilized mimicked as closely as possible typical concrete pore solutions (TCPS), both with and without admixtures. Surface tension of TCPS were also measured as a function of admixture and temperature. Also, TCPS was used to determine the amount of admixture from solution. Turbidimetry was used to examine bubble stability in TCPS with various admixtures.

SDSM&T carried out SEM examination of five (5) field cores representative of low-strength concrete and five (5) field cores representative of high- or normal-strength concrete. A maximum of six (6) additional samples of laboratory mortar, concrete, or aggregate were also be examined by SEM, pending results of laboratory testing of such samples by SDDOT. The emphasis of the SEM examination was to characterize the following microstructural characteristics: size distribution of entrained air; spatial distribution of entrained air; distribution of entrained air with respect to cement paste-aggregate interfaces; and occurrence and distribution of unhydrated cement paste. SDSM&T performed quantitative XRD analyses on a maximum of twelve (12) samples of cement mortar in order to characterize the compounds present and their relative percentages.

Accomplished: This task was accomplished throughout the course of this grant, ~April 1998 to April, 1999. The results are given in the Findings section.

Task 9: Meet with Technical Panel to Discuss Testing and Recommendations for 1998 Season

Task: Both SDDOT and SDSM&T personnel met with the technical panel in Pierre, SD prior to the start of the 1998 construction season. SDSM&T presented results obtained and along with SDDOT gave recommendations for the upcoming construction season.

Accomplished: Mr. Johnston presented several preliminary recommendations to the technical panel in April 1998. As this was approximately the time that the grant was awarded no SDSM&T personnel were involved.

Task 10: Perform Full-Scale Testing

Task: SDDOT will perform the full-scale testing. SDSM&T will not be involved in this task.

Accomplished: This task was not performed due to the success of the 1998 recommendations.

Task 11: Perform Statistical Analysis

Task: SDDOT supplied historical data of SDDOT projects, and SDSM&T personnel performed a statistical analysis of this data to determine if a relationship exists between processing parameters (admixtures, dirty rock, etc.) and low compressive strength concrete.

Accomplished: This task was accomplished during the course of the grant.

Task 12: Prepare Final Report

Task: SDSM&T personnel prepared a final report on the project six weeks prior to project completion. This final report included an executive summary of the literature review, research methodology, research findings, conclusions and recommendations. A single printed copy along with a magnetic copy (Microsoft Word) was submitted to the SDDOT.

Accomplished: A draft final report was submitted in April 1999 to the technical panel.

Task 13: Make Executive Presentation

Task: SDDOT and SDSM&T personnel made an executive presentation of research findings and recommendations to the technical panel upon completion of the project in Pierre, SD.

Accomplished: Mr. Johnston and Dr. Cross presented their findings to the technical panel in February 1999.

Findings

Task 1. Literature Survey

Air Entrainment

Air entraining admixtures have been used for over 50 years to provide resistance to freeze-thaw degradation. NCHRP report 258 [1] summarized the control in concrete at that time. The methods by which air entraining admixtures stabilize the air-void system are complex, but two primary means were identified, reduction in water surface tension and promotion of stable bubble/cement particle aggregates. To achieve both of these means some admixture must remain in solution while some must adsorb to the cement particles. It has been shown that up to 60 % of the original admixture dose remains in solution. Many admixtures also precipitate with calcium ions and these precipitates may also be surface active.

In addition to the type and amount of air entraining admixture added, both the mix design and other components of cement are very important. For instance, increasing the amount of soluble alkalis increases the amount of entrained air and decreases the amount of calcium in the pore solution. Increasing the fineness of the cement decreases the amount of air entrained. The air content increases as the water to cement ration increases, while the air content decreases as the maximum aggregate size increases. The air content also increases when sand is added to the cement.

Since this report was issued in 1983, several changes have occurred in concrete practice. In particular, vinsol resin was used almost exclusively to entrain air in concrete in 1983. The observations used to determine the statements given in the previous two paragraphs were made either for vinsol resin, sodium abietate, lignosulfonates or common surfactants such as sodium dodecylsulfate. However, during the 1990s “synthetic” admixtures became widely used to entrain air in concrete. Shortly after these “synthetic” admixtures began to dominate the market, several states reported low compressive strength values for air entrained concretes.

Contacts with other States

New Jersey

A report by Ricardo Barrios, New Jersey DOT, presents the results of a statistical analysis of low compressive strengths in New Jersey from June-September, 1994. A total of 192 concrete lots were used in the analysis and the results, as stated by Mr. Barrios, are as follows:

"An analysis of variance/ regression performed on 192 Class A concrete lots placed between June and September, 1994, revealed that strengths were significantly affected by two factors. These were the air entraining agent used and the presence of an inspector at the concrete batch plant. Essentially, this data set estimated the mean 28-day compressive strength to be 4600 psi, plus 750 psi if a vinsol resin air entraining agent was used, plus 200 psi if a state inspector was present at the batch plant. Both the air and inspector factors were statistically significant at the 95 % confidence level.... The predominate factor associated with lower strengths is seen to be use of the synthetic air entraining agents." (Italics our own).

Industry challenged these results on the basis of uncontrolled variables but further analysis of Class B and Class B White concrete produced the same trends, although with a lesser magnitude of effect. The effects attributable to the use of vinsol resin were 243 psi and 600 psi, respectively, for Class B and Class B White. A list of summary statistics from the Class B White is shown in Table 1. Interestingly, the White Cement used was a Lehigh low alkali.

Table 1. Strength Data for NJ Class B White Concrete

	Synthetic A.E.A."s	Vinsol Resin A. E. A.'s
Sample Size	201	71
28 day Compressive (psi)	4904	5421
Std. Deviation (psi)	726	572
Minimum Strength (psi)	3215	4185
Maximum Strength (psi)	7920	7345
Range (psi)	4705	3160
Average Air (%)	6	6.5

Delaware

Mr. William B. Brode, DelDOT PCC Supervisor, was contacted with respect to a low compressive strength problem encountered on Project SR 896. In a telephone discussion he indicated that the low strength problem seemed to be directly related to a particular low alkali cement and that low strength problems were by no means pervasive in Delaware. He also stated that Class A concrete (4500 psi) in Delaware requires the routine addition of water reducer, which may be a major factor in the low incidence of strength problems. Although he was unable to provide us with a petrographic report on cores taken from the project, he did state that there was a definite clustering of air bubbles adjacent to the aggregate in samples from low strength concrete. Table 2 presents an interesting tabulation of strength results from the plant which experienced the problem with low strengths. As the production data indicates, the failure rate jumped to an unacceptable 59.46 %. In fact the average 28 day compressive strength when the plant switched to MBAE-90 from using MBVR-C was below the 4500 psi minimum at 4401 psi and dropped 1100 psi below the average of the other three observation periods.

South Dakota

An analysis of a construction project in South Dakota along similar lines to the one from Delaware is shown in Table 3. The project consisted of an urban section in Rapid City, SD including two structures. The concrete used for the mainline pavement was specified as A45 (4500 psi), the same class as that used in the structures. At the beginning of the project, a vinsol resin air entraining admixture was used but was subsequently changed to a "synthetic" admixture during the following year. The resemblance between this project and the one in Delaware is striking with no failing cylinders using vinsol resin and a 50 % failure rate the following year. The same cement source, aggregate and concrete plants were used during both construction seasons. Cores were taken from this project for petrographic analysis where failing strength tests indicated a major problem with the concrete. As in almost every project with failing strengths during the 1997 construction season, no petrographically-determined properties of the concrete could explain the low strength as water-cement ratios, hardened air and aggregate distributions were all nominal.

Table 2. Class A Concrete Produced by J.P. Dugan & Sons

	Observation 1	Observation 2	Observation 3	Observation 4
Production Dates	1/21/93 to 3/16/93	5/1/93 to 10/28/94	8/23/93 to 7/30/94	3/31/95 to 10/27/95
Sample Size	9	29	35	37
Average (psi)	5777	5053	5701	4401
Min (psi)	4720	4000	3430	3350
Maximum (psi)	6720	6760	7690	6430
Std. Dev. (psi)	621	621	908	618
Failing Tests (< 4500 psi)	0	4	2	22
% Failures	0	13.79	5.71	59.46
Average Air (%)	6.4	5.7	6.5	5.6
Average Slump (in)	3.25	3.89	3.81	3.93
Ave Concrete Temp (^{O}F)	71	77	70	79
Cement	Hercules LA	Keystone LA	Keystone LA	Keystone LA
A. E. A.	MBVR-C	MBVR-C	MBVR-C	MBAE-90

Other States

Although documentation is unavailable, reports of low strength problems have been received from Minnesota, Virginia, New York, Michigan and Ohio. Initial reports of low compressive strengths from Virginia and Michigan, although not indicated as a general trend, both involved clustered air bubbles on aggregate faces.

Table 3. Compressive Strength Results on P2016

<table>
<tr><td colspan="5">Project P2016 PCEMS 3760 Campbell Street Rapid City Stanley Johnson</td></tr>
<tr><td colspan="5">A45 Concrete September-December 1996 MBVR AEA 19 Cylinders</td></tr>
<tr><td></td><td>Strength</td><td>Air Content</td><td>Unit Weight</td><td>Slump</td></tr>
<tr><td>Average</td><td>5531</td><td>6.13</td><td>144.6</td><td>3.26</td></tr>
<tr><td>Maximum</td><td>6310</td><td>8</td><td>147.7</td><td>4.5</td></tr>
<tr><td>Minimum</td><td>4650</td><td>5.4</td><td>139.5</td><td>2</td></tr>
<tr><td>Range</td><td>1660</td><td>2.6</td><td>8.2</td><td>2.5</td></tr>
<tr><td>Standard Deviation</td><td>444</td><td>0.58</td><td>1.98</td><td>0.6</td></tr>
<tr><td>C. V. (%)</td><td>8</td><td>9.4</td><td>1.4</td><td>18.5</td></tr>
<tr><td colspan="5"></td></tr>
<tr><td colspan="5">A45 Concrete April-September 1997 Conchem AEA 33 Cylinders</td></tr>
<tr><td></td><td>Strength</td><td>Air Content</td><td>Unit Weight</td><td>Slump</td></tr>
<tr><td>Average</td><td>4463</td><td>6.7</td><td>142.7</td><td>3.05</td></tr>
<tr><td>Maximum</td><td>5750</td><td>10.8</td><td>146.7</td><td>5.5</td></tr>
<tr><td>Minimum</td><td>3310</td><td>5</td><td>134.9</td><td>1.75</td></tr>
<tr><td>Range</td><td>2440</td><td>5.8</td><td>11.8</td><td>3.75</td></tr>
<tr><td>Standard Deviation</td><td>615</td><td>1.44</td><td>2.97</td><td>1.01</td></tr>
<tr><td>C. V. (%)</td><td>13.8</td><td>21.6</td><td>2.1</td><td>33.2</td></tr>
</table>

Interfacial Structure of Concrete

Because the instances of low compressive strength in air entrained concrete seems to relate to the clustering of air bubbles in the vicinity of the aggregate particles, the relevant literature concerning the formation of the interfacial structure was identified. Since the late 1940s a separate region has been shown to exist between the aggregate surface and the bulk concrete matrix. This region has come to be known as the interfacial transition zone (ITZ). Depending on the interface studied, the ITZ is anywhere from 20 to 40 μm (0.005 – 0.01 inches) in thickness [2]. The microstructure of the ITZ has been studied primarily by back-scattered SEM. Two primary components of the ITZ microstructure have been identified. At the aggregate surface a thin layer (~1 m thick) of reaction products form. This is often called the duplex film, which consists of calcium hydroxide on the aggregate side and C-S-H on the paste side. The presence of calcium hydroxide seems to depend on the type of aggregate and whether or not the aggregate has a continuous layer of water coating it. Further from the aggregate surface, the ITZ consists of paste which is affected by the presence of the aggregate 'wall' at the interface [3]. The primary effect of the wall is on the packing efficiency of the cement grains. As the wall is approached the amount of empty (non-cement filled) space approaches 100 %, causing a film of empty space at the aggregate surface. After reaction begins this means that the porosity of the ITZ is very high in the vicinity of the interface. Porosity values of 2-3 times the bulk porosity are not uncommon. Also, the smaller cement grains tend to end up near the aggregate, at least in the first ~20 m, while larger cement grains are the main cement constituent from ~20-50 m from the interface. The cement grains will only segregate as described if the aggregate is present during the mixing of the concrete. Because of this segregation the region with the smaller particles reacts faster than the region with the larger or the bulk region. Also, the region adjacent the aggregate surface has a higher water to cement ratio than the bulk paste. Experiments have shown that mixes with lower water-to-cement ratios and/or higher aggregate-to-cement ratios promote more efficient packing of the cement grains near the aggregate and hence smaller interfacial zone widths. Higher water-to-cement ratios and/or lower aggregate-to-cement ratios cause a bigger interfacial transition zone. Other common occurrences in the ITZ are that the calcium hydroxide formed may become oriented and that ettringite formation is enhanced.

Very little experimental work has been performed to assess the effect of chemical admixtures on the ITZ. One paper has been published which examined the effect of a naphthalene-sulphonate superplasticizer on a Portland cement with carbonate rock aggregate. This work found little difference in the thickness of the ITZ or in the orientation of calcium hydroxide particles within the ITZ [4].

Mineral admixture addition and its effect on the ITZ has been studied extensively, particularly for the addition of silica fume. These small silica particles reduce the porosity of the ITZ and also reduce the amount of calcium hydroxide formed. Silica fume is thought to promote more efficient packing within the ITZ which leads to lower local water-to-cement ratios in the ITZ.

In general, the interfacial transition zone (see Figure 4) is weaker than the bulk cement paste. This has been investigated for a variety of systems by micro-indentation hardness measurements. Figure 5 shows micro-indentation hardness measurements of an ITZ [5]. This figure shows that the microhardness decreases as the aggregate is approached. This decrease is most likely due to the increased porosity and the increase in calcium hydroxide. In many circumstances, the

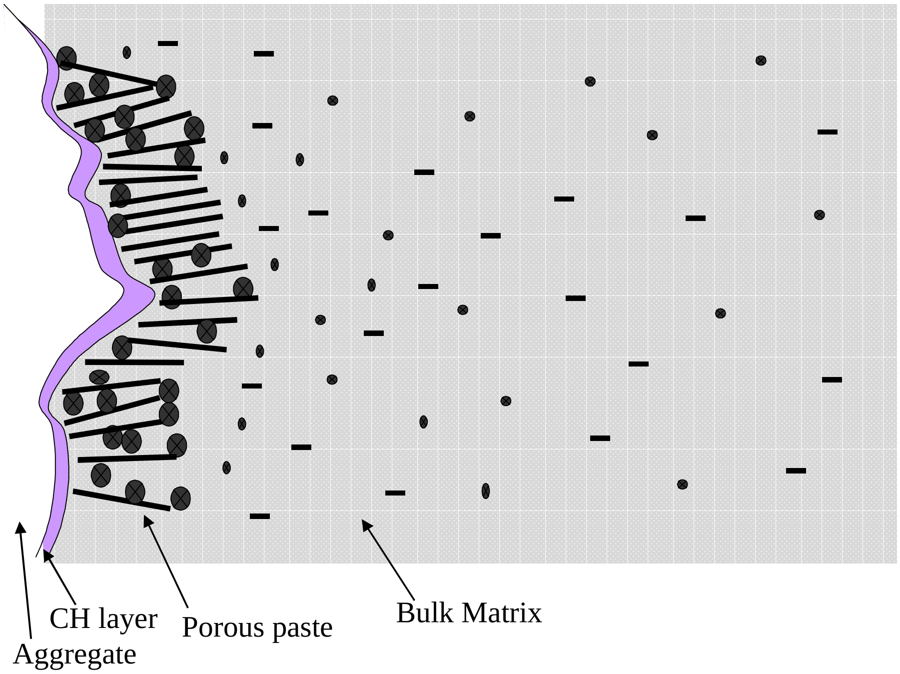


Figure 4. Structure of the interfacial transition zone. After Bentur and Odler, 1996 [4].

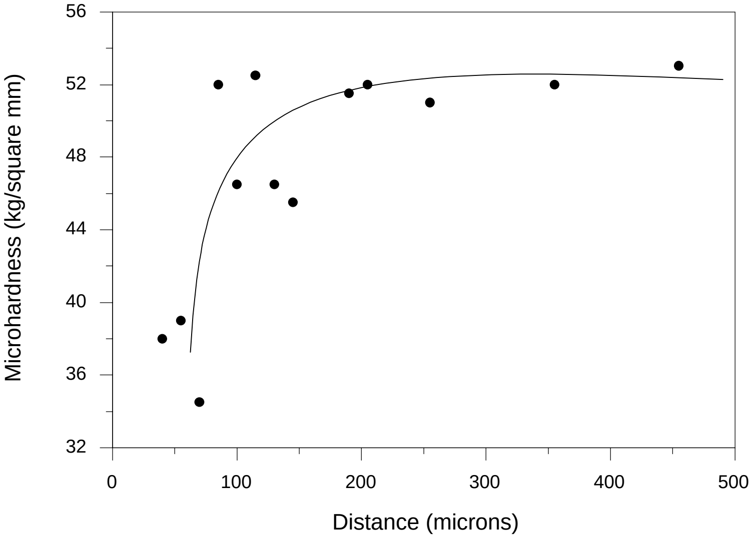


Figure 5. Microhardness versus distance from reinforcement. After Cross et al., 1999 [5].

hardness is directly proportional to the yield strength of a material. Thus, the formation of the ITZ can lead to a weakened zone in the vicinity of the aggregate surface which may have a deleterious effect on the strength of the concrete composite material.

Effect of Temperature on Concrete Strength

As the low strength problem in South Dakota seemed to be worse in the summer months, the effect of temperature on concrete strength was searched for in the literature. Only one paper was found that dealt with drops in concrete strength in the summer [6]. In this work summer conditions were simulated by heating the aggregate to various temperatures (20, 35 and 70 C) and having the cement temperature at 70 C. This latter temperature was chosen because "cement is often delivered on sites at this relatively high temperature in summer". It was found that when the aggregate temperature was 70 C the 28 day compressive strength dropped about 15 %. Also, although there was an increased water demand, this increase did not fully account for the strength drop. When the aggregate temperature was 35 C, there was essentially no drop in strength.

Foam Drainage Testing

One of the goals of this project was to identify a test which can be used to evaluate the concrete system to quickly determine if the concrete will be of sufficient strength. Typical practice is to measure the compressive strength by ASTM C-39 [7]. This test is obviously the best method if time is no object but 28 day curing is necessary to determine if the concrete is sufficiently strong. One test which may offer the possibility of evaluating the concrete system in a short period of time is a foam drainage test. The use of foams to test air entraining admixtures goes back at least to the 1950s when Bruere utilized a cylindrical flotation apparatus to examine stable foams formed by several air entraining admixtures. Due to their occurrence in a wide variety of systems, foams have received a considerable amount of study. Two books, one by Bikerman [8] and the other by Exerowa and Kruglyakov [9], have been exclusively devoted to foams and foam films. With respect to concrete and foams, Gutmann [10] utilized a simple, cheap method to test foams from air entraining admixtures. A standard kitchen blender was used to put air into water and the resultant foam was poured into a graduated cylinder and the level of water drained from the foam was measured after 1 hour. Gutmann [10] used 10 admixtures and measured the percent of foam drained after 1 hour and the bubble density. While this test protocol showed some interesting results, there are two major problems with its use. First, and most vexing, is that the test does not consider the interaction of the admixture/foam with the cement particles and hence does not adequately simulate a concrete environment. This limitation is not an intrinsic limitation of the test but rather a limitation imposed by Gutmann's protocol. Second, the use of only one time (1 hour) does not allow the determination of the kinetic nature of the foam drainage, which may be useful in differentiating between admixtures. It should be noted that Gutmann [10] also observed mass coalescence of air bubbles at the aggregate/paste interface in several of his specimens.

The treatment of the kinetics of foam drainage in a gravitational field has been performed for many years. At least 20 empirical equations have been developed, while more recently the type of foam and the films between two bubbles and the borders at the contact of several bubbles have been taken into account. Typically there is an induction time before the water begins draining from the foam. The length of the induction time depends on the liquid distribution between films and borders, the foam column height and the surfactant concentration and type. For this work, several kinetic equations will be evaluated and the equation that best fits the data will be utilized.

The equation to be used is:

$$V_d = V_0 - \frac{1}{k} * t \tag{1}$$

V_d is the amount of liquid drained from the foam at time, t. V_0 is amount of liquid in the foam at the start of drainage and is parameter found from fitting the equation to the data. The variable k is a constant found from fitting the equation to the data. This equation has been shown to work well for the final stage of drainage. To determine V_0 and k, V_d is plotted versus 1/t. When plotted this way a linear relationship results such that, V_0 is the intercept and –1/k is the slope. This equation was first proposed by Erbring and Peters [8], and is expected to work well, although at very short times it loses physical meaning. This should not be a problem as, due to the manner in which the tests are run, the initial value for the time is approximately 20-30 seconds. The best fitting equation was determined to be the equation which yielded the highest average adjusted Pearson product-movement correlation coefficient.

Task 5. Study Database of SDDOT Projects

A comprehensive survey of Class A45 compressive strength results for the years 1997 and 1998 was completed. The survey encompassed the months from January through September to determine seasonal trends and compare the number and magnitudes of compressive strength failures in these years. The results of this survey are shown in Table 4 and show a favorable reduction in the incidence of low strengths during the 1998 construction season. The primary change made in our Class A45 concrete specification this year was the elimination of non-vinsol resin air entraining agents from use. In addition, the policy of using water reducers in situations where compressive strengths were not sufficiently high or failing tests were occurring was continued. The overall reduction of failures from almost 15 % in 1997 to 8.77 % this year may not seem especially satisfying but the almost complete elimination of catastrophic low strengths (arbitrarily assigned to strengths of 4000 psi or less) means that we did not have the major problem of structural inadequacy in 1998 that we had in 1997. The data set has been broken out into projects including and excluding Minnehaha County in the 1998 results to clarify a trend which was not apparent in the 1997 data. Fully half of the 1998 failing strength tests originated from concrete plants in Sioux Falls. In fact some portion of these failing tests are associated with continued use of synthetic air entraining agents until as late as June, 1998. Although it is impossible to break out which failures occurred with synthetics and which with vinsol, we do know that concrete delivered to a project was produced at a plant that had no vinsol resin available at the time. In 1997 40 % of the failing tests were catastrophic and a significant number of these were characterized by an alarming inability to gain strength over time. In 1998 only 12.5 % of failing tests were catastrophic and the vast majority of these only slightly lower than 4000 psi. If Minnehaha County is excluded, there were only 2 tests lower than 4000 which represents 10 % of failing tests in the rest of the state. No data have been assembled to determine what our "normal" rate of failing strength tests is during a regular construction season but the problem seems to be moderating with the changes already made. Figures 6 and 7 illustrate these trends and show that, although the low strength problem may not have been completely solved in 1998 there was a substantial improvement. Considering that the implementation of the use of vinsol

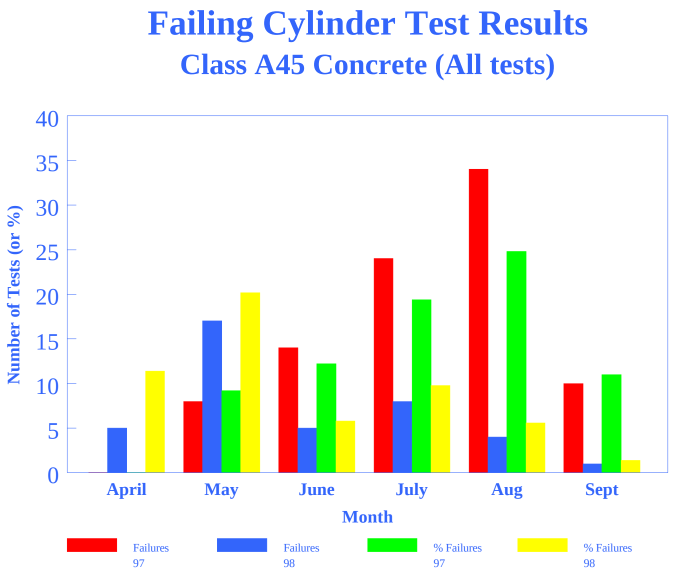


Figure 6. Comparison of failing A45 concrete tests 1997 and 1998.

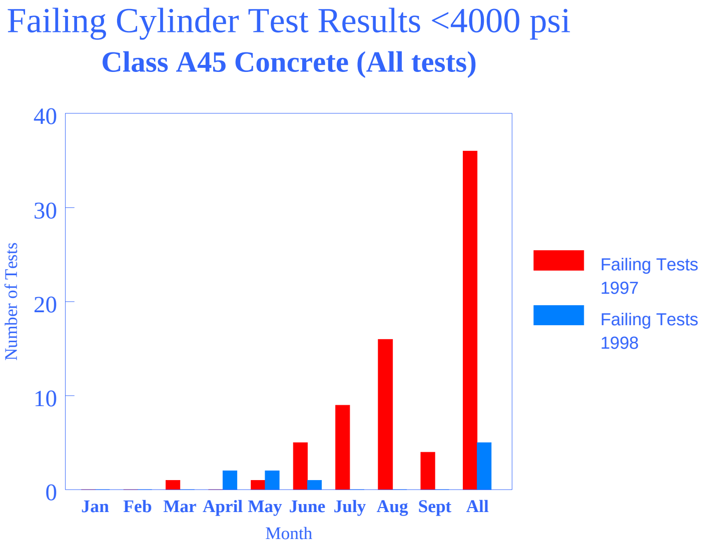


Figure 7. Comparison of average of failing tests by month 1997 and 1998.

resin air entraining agents was not completed until June, 1998 it is striking that the highest failure rate occurred in May, 1998 and dropped off during the heat of the summer whereas August was the month of most failing strength tests in 1997.

Table 4. Comparison of A45 Failing Strength Tests for 1997 and 1998

Month	Failures		Failures without Minnehaha 1998	Failures < 4000 psi					
	1997	1998		1997		1998		1998 w/o Minnehaha	
				No.	Ave	No.	Ave	No.	Ave
January	0/7	0/10	0/6	0		0		0	
February	0/10	0/5	0/3	0		0		0	
March	1/12	0/5	0/5	1	3380	0		0	
April	0/30	5/44	3/42	0		2	3760	1	3960
May	8/87	17/84	4/51	1	3480	2	3845	0	
June	14/115	5/86	4/66	5	3860	1	3960	1	3960
July	24/124	8/82	6/60	9	3847	0		0	
August	34/137	4/71	3/60	16	3664	0		0	
September	10/91	1/69	0/59	4	3890	0		0	
All	91/613 (14.9 %)	40/456 (8.77 %)	20/352 (5.68 %)	36	3696	5	3834	2	3960

It is interesting to compare what Delaware observed on one project to what occurred in 1997 in South Dakota. The failing tests in Delaware were associated with one particular brand of cement (Keystone Type II LA), similar in general composition to what we specify for concrete in South Dakota . When the plant switched from vinsol resin to a rosin-based air entraining agent, MBAE-90, with no other changes in ingredients, compressive strengths fell precipitously and the average strength of concrete being produced for Delaware DOT in this plant was below the specified 4500 psi minimum. Separate laboratory testing of the mix by Delaware Department of Transportation yielded an average of 3570 psi for MBAE-90 and 4820 psi for MBVR, confirming the field results. Perhaps the low alkali content of these cements is somehow contributing to the problem.

Task 8: Complete Laboratory Testing

Laboratory Concrete Testing

Purpose: Laboratory testing of concrete specimens and cement mortar cubes was performed to assess the effect of aggregate type, mix design, air entraining admixture and temperature on properties and compressive strength of concrete similar to that used for paving, precast and structural applications. This testing assessed the cement (cause 1), harshness of mix design (cause 2), air entraining admixtures (cause 4), temperature (cause 5), and mixing time (cause 8).

Method: Laboratory testing was completed on both cement mortar cubes and on concrete specimens using a variety of different air-entraining agents. The cube tests were conducted with a modified ASTM C109 [11] protocol where various air-entraining agents were added to the mix water prior to mixing. Air content of the mortar was measured for each batch and a nominal target air of 18 2 % was maintained throughout. Control batches were also made for each day's mixing to insure relative uniformity. An additional set of batches was also made using heated sand (49 C) to yield a mortar temperature of ~30 C. Statistical analysis of 3, 7 and 28 day strength results yielded no significant trends. An additional series of batches using field samples of cement from various construction projects were also tested to determine the effect of mixing time on 3 and 7 day strengths. Standard ASTM C109 cubes were made with each cement and another parallel set made without including the 1 minute intermediate mixing cycle. Again, no statistically significant difference between the two sets was apparent. Further testing with cement mortars was discontinued and all subsequent testing was done on concrete specimens. One potentially significant observation was made, however, during these mortar tests. Vinsol resin mortars entrained air during the initial mixing step after sand was added to the mixer. None of the other air entraining admixtures began entraining air until after the rest period was over and mixing commenced again.

Results: A total of 109 different mixes using 11 different combinations of coarse and fine aggregate and 6 different air entraining agents combined into groups of 8 mixes using the same ingredients were tested for air, slump, unit weight and compressive strength at 7 and 28 days. The mix types are illustrated in Table 5. Aggregate samples were obtained in the normal manner from around the state and subjected to routine sampling and testing prior to being incorporated into concrete mixes. The same cement, Dacotah Type I-II LA, was used for all concrete although three separate shipments of cement were used during the course of the laboratory testing. ASTM C192 Standard Practice for Making and Curing Concrete Specimens in the Laboratory [12] was used to produce concrete specimens where appropriate. The only exception to this was a three minute mix where the concrete was dumped and test specimens made after the initial mixing without the normal 3 minute rest period and 2 minute remix. The heated mixtures were obtained by heating the aggregate in an oven to approximately 49 C overnight prior to use to yield concrete with a temperature ~32 C upon discharge. An initial analysis of the strength data showed a significant difference in strength between specimens made with the third shipment of

Table 5. Laboratory Concrete Mixes

Mix	Normal	Hot
1. ASTM C192	17	11
2. 3 Minute Mix	17	11
3. Water Reducer Mix	17	11
4. Non-Air Entrained Mix	14	11

cement and those made with the first two shipments. These results are tabulated in Table 6, separated into various mix types. None of the mixes made with the last shipment involved the use of heated aggregate so that hot mixes are excluded from the comparison. The most interesting aspect of this effect is its limited nature-not all the mixes had a statistically significant difference in 28 day strength between cements. The control mixes without air entraining agent only differed by 91 psi indicating that there was little intrinsically greater potential for strength development with the second cement. Addition of a water reducing admixture also yielded a similar result with a difference of only 16 psi. Examination of the effect of the water-cement ratio, w/c, showed a statistically significant difference between the two groups, i.e. the average w/c for cement 1 mixes was lower than for cement 2 and therefore, everything else being equal, the 28 day strengths should have been higher not lower. Cement is obviously a contributing factor to strength development but these results raise the possibility of lower strengths being the consequence of a negative interaction between the cement and other ingredients in the concrete. Cement 2 mixes, in every case, had a lower air content than cement 1 mixes no matter the mix type. Since the dosage of air entraining agents was held constant for all mixes this is consistent with a different response from cement 2 compared to cement 1. This difference could explain the lower strength results with air entraining agents added except for the facts that the difference in air content was not statistically significant for Type 1 mixes and the Type 3 mix compressive strength averages differed only by 16 psi even though their air contents were significantly different. To insure that these trends were not being biased by aggregate type, the same analysis was rerun on quartzite mixes only without changing any of the results.

As a further means of investigating whether the cements were truly different, a subset of mixes using the same coarse and fine aggregate and the two cements were extracted from the database. First, the 28 day compressive strengths of control mixes with no entrained air were plotted against their water-cement ratios as shown in Figure 8. The response to increasing w/c values was strongly linear for both groups with R^2 values of 0.995 and 0.999 which offset the small sample size. Heating the aggregate prior to mixing caused an average reduction in strength for all mixes of about 430 psi, part of which is explainable by an 8 % increase in water demand. Higher concrete mix temperatures are known to affect compressive strength adversely and could contribute to low compressive strengths during the summer months. Interestingly, the effect of heated aggregate on strength was not as pronounced in mixes with vinsol resin air entraining agent as compared to synthetic air entraining agents. Cement 1 mixes with vinsol averaged a 333

Table 6. Comparison of Mixes Using Different Cement Shipments

Mix Type	Strength (28 days)		Air (%)		Slump (inches)		Unit Weight (lbs/ft^3)	
Cement	1	2	1	2	1	2	1	2
1 (Ave)	4776	5154	6.50	5.94	4.15	4.07	143.28	143.56
St.Dev.	471	111	0.69	0.62	0.27	0.12	1.70	1.26
Diff	378		0.560		0.480		0.277	
Prob p	0.034		0.102		0.648		0.705	
2 (Ave)	5065	5546	6.43	5.63	4.03	3.82	143.34	144.17
St.Dev.	315	254	0.69	0.33	0.25	0.19	1.05	0.52
Diff	481		0.80		0.20		0.83	
Prob p	0.003		0.007		0.074		0.05	
3 (Ave)	5436	5452	6.39	5.80	4	4.04	143.72	144.06
St.Dev.	274	254	0.58	0.17	0.20	0.09	1.41	0.41
Diff	16		0.59		0.04		0.34	
Prob p	0.903		0.012		0.636		0.489	
4 (Ave)	6735	6643	2.83	2.20	3.88	3.88	148.50	149.05
St.Dev.	461	215	0.39	0.37	0.41	0.32	1.06	0.98
Diff	91		0.63		0.00		0.55	
Prob p	0.623		0.029		1.000		0.391	

psi drop with heated aggregate whereas synthetics averaged 474 psi. The strength loss for vinsols was not significant at the 95 % confidence level ($p = .112$), partly due to small sample size, but the strength loss for the synthetics was highly significant ($p < .0006$) indicating that under conditions where high concrete temperatures could be a problem, vinsol performs better than other air entraining agents. During the mixing process, mixes with vinsol were noticeably more workable and seemed to require less water and mixing time.

The database used for analyzing factors contributing to lower compressive strengths was not developed based on a factorial design as it was necessary to accommodate ASTM C233 testing of air -entraining admixtures from the 1997 construction season in addition to testing for effects. Of the total of 109 concrete mixes tested, 16 were made with Minnekahta Limestone coarse aggregate, 8 with Summit dolostone and the remaining with Sioux Falls Quartzite. Statistical analyses were adjusted to minimize effects due to the variety of mixes. The final 29 mixes employed the same coarse and fine aggregate with the only planned variable being the air-entraining admixture used but this was somewhat confounded by the effect of the cement, as shown in Table 6, as the third shipment of cement was used in all these mixes.

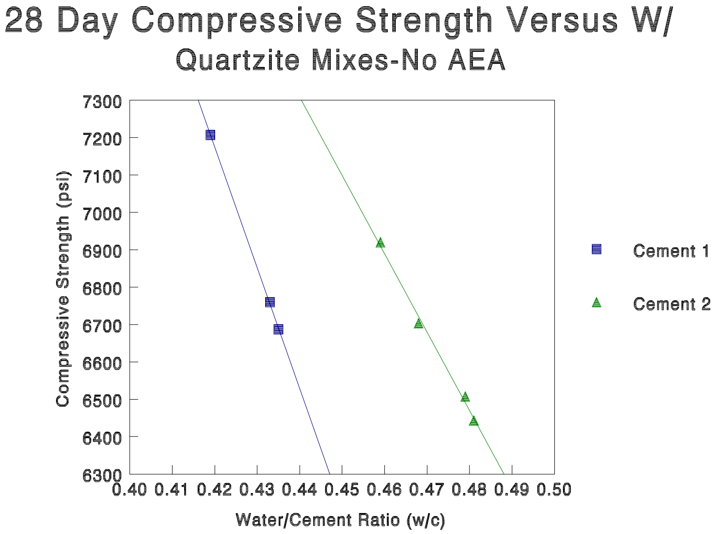


Figure 8. Plot of 28 day strength vs. w/c for concrete made with no air entraining admixture.

The first effect looked at was the possible contribution of dirty coarse aggregate to any strength problems. During the course of preparing the aggregate for inclusion in the concrete mixes both the fine and coarse aggregate were examined for fines and dirt . Although all coarse aggregate had extensive rock dust, only one source can be characterized as containing a significant portion of what may be considered dirt-a limestone aggregate with a significant quantity of Opeche or Spearfish shale in the sample. Upon mixing, this shale would disintegrate and some of it would smear onto the limestone, possibly affecting the bond with the cement matrix. A t-test comparison between the series made with this aggregate and the prior and following series made with quartzite showed no significant difference in strength. Although the limestone mixes were slightly lower in compressive strength, this by itself is not surprising as the limestone is a weaker aggregate. Ironically, the dirty aggregate source had no failing compressive strength tests for the 1997 construction season.

The next mix type examined in the database was the control mixes with no air entrainment. These were used as a basis of comparison for all other mixes. Since there were no significant differences between cements used in these mixes, all results were included in the analysis, at least on a preliminary basis. Regression analysis of this data (n=11) was confined to quartzite mixes at room temperature to minimize uncontrolled variance. The analysis yielded only three factors strongly associated with the 28 day compressive strength-cement factor, water-cement ratio and fineness modulus of the coarse aggregate. None of the other variables met the $p < 0.15$ requirement for inclusion into the model. The initial model had an $R^2 = 0.775$ with two points identified as suspect. The first was an outlier and the second had large leverage on the model. Examination of the database showed the outlier had a different cement factor than all the other mixes and was solely responsible for its being significant. This data point was thrown out and the regression analysis repeated without including the cement factor as an independent variable. The result was an $R^2 = 0.772$ for this iteration with the same point above identified as having large leverage again having large leverage, being an outlier and having large influence. A check of the data showed that the water-cement ratio for this mix, at 0.406, was almost two standard deviations from the mean for the data set. Eliminating this point yielded an $R^2 = 0.960$ (corrected 0.946), $p < 0.00001$ and $F = 72$. The fineness modulus of the coarse aggregate had a positive effect on strength and the water-cement ratio a negative one, as expected, with ¾” maximum aggregate size.

The next series of mixes examined excluded those mixes made from the final cement shipment. Again quartzite was the only aggregate used. These mixes comprised the standard laboratory mixing procedure of 3 minutes mixing, 3 minutes rest and 2 minutes additional mixing time. Only room temperature mixes were included in the analysis which revealed no discernible relationship with any mix factors. The really interesting effect in the analysis was the fact that the w/c ratio, the most significant negative factor in the control mixes, positively correlated with higher 28 day strengths. An analysis of the 3 minute mix series yielded the same lack of correlation with the same positive relationship between strength and w/c ratio, the primary difference being an overall higher average strength for the 3 minute mix series as compared to the standard series although this was not statistically significant. A similar analysis of the two hot mix series yielded substantially similar results although the 28 day strengths for the 3 minute mixes were significantly higher than the standard mixes (4616 psi versus 4299 psi, $p = .02$). A model based on both types of mixes and both temperature regimens ($n = 32$) yielded an $R^2 = 0.608$, $p < 10^{-5}$ with only temperature and mix time robust enough to include in the model. Neither air nor w/c ratio could be included which implies the major effector of compressive strength besides temperature and mix time was not one of the independent variables examined.

Analysis of the standard mixes with water-reducer added provided the results expected being directly comparable to the control mixes. The primary predictor of cement strength was the w/c ratio which correlated negatively with strength ($R^2 = 0.625$, $p = .0016$). Air content was the only other significant factor. Interestingly, when both room temperature and hot mixes were included in the analysis, temperature was not a significant factor ($R^2 = 0.674$, $p = .06$). Excluding the heated mixes did not affect the model results.

Although these laboratory mixes do not provide incontrovertible evidence of the factors effecting strength, the results are intriguing with regard to those factors which do not correlate with strength, even though they should. For the mixes fabricated with cement 2, the w/c ratio correlated negatively with strength for all mixes. Mix time was also negatively correlated with strength with the difference between standard and 3 minute mixing 492 psi ($p < .003$). Air was not a significant factor but slump for the standard mix was 0.25 % greater ($p < .013$). Overall, the data are confounded by the difference in cement but the fact that mix procedure directly affected strength is difficult to explain. There was no response difference between vinsol resin mixes and the other AEAs tested with respect to mix time. A comparison between standard mixes made with cement 2 and standard mixes made with cement 2 and water-reducer showed a normal trend in that the average strength of the latter was 298 psi higher ($p < .015$). The same comparison between 3 minute mixes and water-reduced mixes yielded an opposite result with the average of the 3 minute mixes 92 psi higher with no significant difference ($p > .5$) between the two. Air content for the two groups was not significantly different.

The one factor which stands out in these analyses is the anomalous response of air-entrained mixes with cement 1. No matter which mixing procedure was employed, the strength development for these mixes was adversely affected indicating an interaction between the cement and the air system which reduced strength. Addition of a water-reducing admixture effectively eliminated the anomaly. Cement 2 did not display this behavior but it did provide an insight into the difference mixing procedure can have on strength development. Normally, increased mixing time is considered desirable and beneficial to the strength development of the concrete. The fact that the 3 minute mixes with cement 2 had higher average 28 day strengths than the water-reduced mixes with this cement indicates that the further mixing time is permitting an interaction to occur that has a negative effect on the concrete which is offset by adding a water-reducer.

Maxim Mixes

One of the potential sources for the low compressive strength problem was the possibility that the relatively harsh nature of the standard Class A45 mix was creating problems with dispersion and strength development. To address this, a series of concrete mixes were fabricated and tested by Maxim Technologies, Inc. using materials supplied from the three largest central concrete plants in South Dakota. Two of the series incorporated Sioux Quartzite as the coarse aggregate and the third employed Minnekahta Limestone. Both cement and sand content were varied in the mixes with vinsol resin air entraining agent used in all mixes.

The cement content of each series was adjusted downward from the nominal amount used for a Class A45 mix in 50 lbs/yd^3 decrements while the sand content was varied from the standard 40 % to 50 % in 5 % increments. The results of these tests are shown in Table 7. Analysis of the data did not support the contention that the high cement contents were adversely impacting strength, nor did it indicate that a mix with 40 % fine aggregate was substantially lower in strength than the mixes with higher sand content. In fact, there was no statistically significant difference between any of the three sand series with respect to air, w/c ratio, 28 day compressive strength and unit weight. Examining the quartzite mixes separately did not change the results significantly, although the unit weight for the 50 % sand mixes was significantly lower than the 40 % mixes at the 95 % confidence level. The same analysis applied to cement content yielded the expected increase in strength with increasing cement content for the quartzite mixes but not for the limestone mixes, where an opposite trend was apparent (see Figure 9). The most interesting aspect of the limestone mixes was the fact that they did not meet the requirements of ASTM C192 Standard Practice for Making and Curing Concrete Specimens in the Laboratory. The moisture content of the sand was well above the slight excess above absorption allowed by the procedure and averaged about 5 %.

The most striking effect in all mixes was that of air content, especially with regard to quartzite mixes. The compressive strengths fell of significantly, independently of cement content for quartzite mixes with air contents greater than 7.7 %. The trend with limestone mixes, though not as obvious, indicated that air contents > 7.5 % degraded compressive strength significantly. Regression analysis of all mix data identified cement content, air content and water-cement ratio as the three most significant determinants of compressive strength. Since high air contents have a disproportionate effect on strength as the air content approaches the specification limit of 8%, one relatively simple measure to help alleviate potential low strength problems is to reduce the maximum allowable air content in all concrete mixes to 7.5%. Figure 10 illustrates the trend for all Maxim mixes and lends support to the inherent benefit lowering the maximum air content would provide in insuring no recurrence of unacceptably high levels of failing compressive strengths.

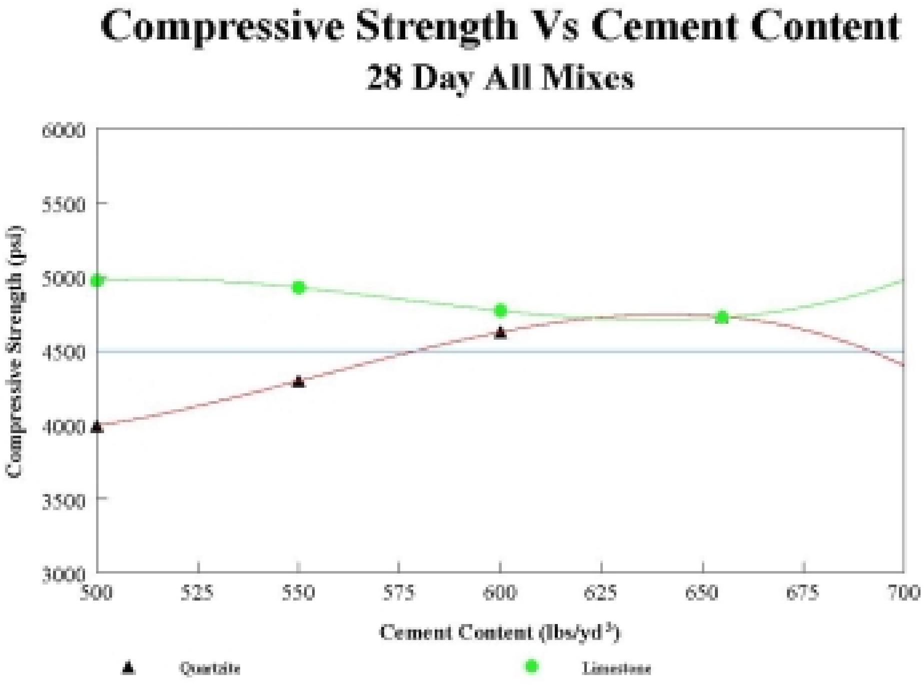


Figure 9. Compressive strength of Maxim mixes as a function of cement content.

Table 7. Maxim Mix Data

Supplier	Ace Redi-Mix (Sioux Quartzite)											
Cement (lbs/yd^3)	655			600			550			500		
Sand (%)	40	45	50	40	45	50	40	45	50	40	45	50
Air (%)	8.0	7.4	8.0	7.0	7.6	7.5	8.0	7.3	8.0	7.4	7.5	8.1
Unit Wt. (lbs/ft^3)	138.4	140.6	135.7	141.9	140.8	140.8	139.7	141.4	140.1	141.7	141.0	139.0
Strength (psi)	4733	4387	4120	4727	4650	4767	4373	4933	4456	4467	4487	4107
Supplier	Birdsall Sand and Gravel (Minnekahta Limestone)											
Cement (lbs/yd^3)	670			620			570			520		
Sand (%)	40	45	50	40	45	50	40	45	50	40	45	50
Air (%)	8.1	8.0	7.5	7.2	8.0	7.5	6.8	7.8	7.6	7.0	7.8	6.5
Unit Wt. (lbs/ft^3)	136.3	137.5	139.9	140.4	137.1	140.6	139.6	140.1	140.9	142.2	141.6	142.5
Strength (psi)	4127	4600	5290	5017	4343	5080	5170	4640	4827	4777	4800	5217
Supplier	Concrete Materials (Sioux Quartzite)											
Cement (lbs/yd^3)	655			600			550			500		
Sand (%)	40	45	50	40	45	50	40	45	50	40	45	50
Air (%)	6.6	6.5	7.6	7.3	8.0	7.9	7.8	7.9	7.8	8.0	7.8	8.0
Unit Wt. (lbs/ft^3)	143.0	142.6	139.7	140.3	137.1	138.0	139.8	138.1	136.8	140.1	137.7	135.9
Strength (psi)	5090	5103	4957	4647	4063	4230	3850	3677	3583	3373	3343	3467

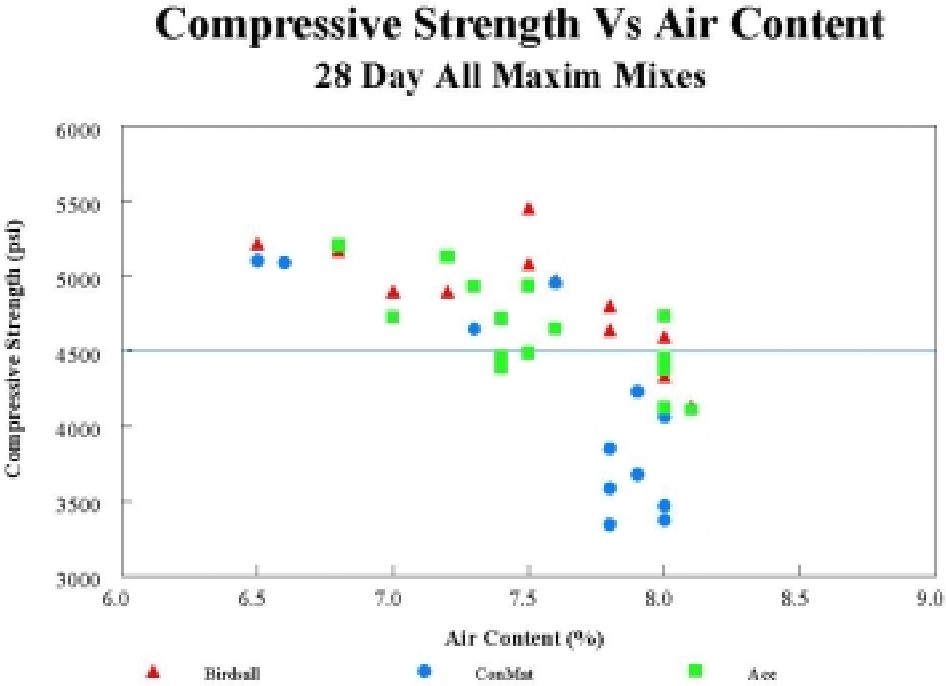


Figure 10. Compressive strength of Maxim mixes as a function of air content.

Foam Drainage Testing

Purpose: Foam drainage testing was performed to give a simple test by which the formation of the air-void system could be examined. This test was preferred over turbidimetry and rheometry. The drainage of the three-phase foams gave considerable differences depending on the air-entraining admixture used. This method therefore gives a very good method for comparing the air bubbles formed in cement/air/air entraining admixture systems. This test assessed, primarily, air entraining admixtures (cause 4). Also, the cement (cause 1) and temperature (cause 7) were examined to a lesser extent.

Method: Foam drainage tests were conducted in the following manner. First, 300 ml of water (tap water unless otherwise noted) was measured. This water was placed in an Osterizer model 625 blender. 10 ml of air entraining admixture was added concurrently with 5 grams of cement. It was found that adding the admixture at the same time as the cement and adding the admixture prior to the cement gave equivalent results. Adding the cement first produced different results, particularly for vinsol resin type admixtures. The use of 5 grams of cement was arbitrary. The test results are somewhat sensitive to the amount of cement particularly for vinsol resin based admixtures. For instance, 4 grams of cement in the foam test with Adair 1800 exhibited about 100 ml of water drained after 1 minute, compared to about 20 ml when 5 grams of cement were used and no drainage after 1 minute when 6 grams of cement were used. The choice of 5 grams was made due to the balancing of the slow drainage for the vinsol resins with the much faster drainage for the synthetic admixtures. The mixing of the cement concurrent with the admixture was done to mimic as closely as possible the field practice for the mixing of admixtures with cement. The admixture and cement were allowed to sit undisturbed in the blender for two minutes. After this two minute period for adsorption and equilibration, the blender was turned on at a medium setting for 10 seconds. After 10 seconds of blending air into the solution, the blender was turned off and the resultant foam was poured into a 1000 ml graduated cylinder. This cylinder was 6 mm in diameter, or 28.3 mm^2 in cross-sectional area. The drainage rate is expected to be a function of the cross-sectional area of the foam, so all graduated cylinders used had the same cross-sectional area. The position of the foam/water line (in ml) was recorded as a function of time. It was impossible to record the position of the line for times less than 20-30 seconds due to the nature of the test and the speed of drainage for those admixtures that drained in a very short period of time. The amount of water drained for each experiment as a function of time was fit to the four equations discussed in the literature survey. It was found that the model of Erbring and Peters [9] (equation 1) provided the best fit for most of the data. In addition, the value found for V_0 was less than 300 in all cases further showing the validity of using this model. Examination of the data indicates that V_0 is more accurately thought of as the amount of water drained from the foam rather than the amount of liquid in the foam at the start of drainage. Two other parameters can be derived from V_0. These parameters are the percent of water drained, %drained, which is:

$$\%\text{drained} = \frac{(300 - V_0)}{300} * 100\% \qquad (6)$$

The 300 in equation 6 comes from the initial amount of water added to the system. This is essentially what Gutmann [10] did to compare the air entraining admixtures that he tested except that Gutmann used a standard time of 1 hour for the determination of V_0. The second parameter that can be found from V_0 is the percent of water in the foam, %wif, which is:

$$\%\text{wif} = \frac{300 - V_0}{\text{Foamheight} - V_0} * 100\% \qquad (7)$$

The variable foamheight is the height of the foam (in ml) at the end of the experiment. The variable %wif will be used to compare the foams formed by the air entraining admixtures. %wif will be used rather than (foamheight - V_0) to normalize for the effect of the different air bubble sizes between the various admixtures.

Results: The following foam drainage experiments were performed for this work. First, the drainage of the foams formed by the air entraining admixtures, MBVR, Adair 1800, Daravair 1400, Darex II, Daravair1000, Conchem Air, and MBAE 90, in the absence of cement particles was determined. These tests were performed in tap water for all of the admixtures and in deionized water for MBVR and Daravair1000. Second, the drainage from foams of the same air seven admixtures listed above was determined with cement particles present. Several different cement samples were used. These cements were: cement 1 and cement 2 discussed in the concrete mixes section of the laboratory concrete testing section above; and 4 dated job cements obtained from various places and times within the state during the past 4 years. These job cements will be identified in more detail later in this section. In addition to the testing with cement samples, several tests were performed with 1 gram of powdered quartzite added to the cement. These tests were performed to simulate the presence of aggregate in the mix. Also, samples of the cement 1 and cement 2 were mixed with Na_2SO_4 and K_2SO_4 to simulate the presence of excess soluble alkali cations in the cement. Finally, foam drainage tests were performed with the cement heated to 65 C prior to its introduction into the blender.

Foam Drainage without Cement

To begin the foam drainage testing the behavior of the air entraining admixtures was determined in the absence of cement. Figure 11 shows some typical results of these tests.

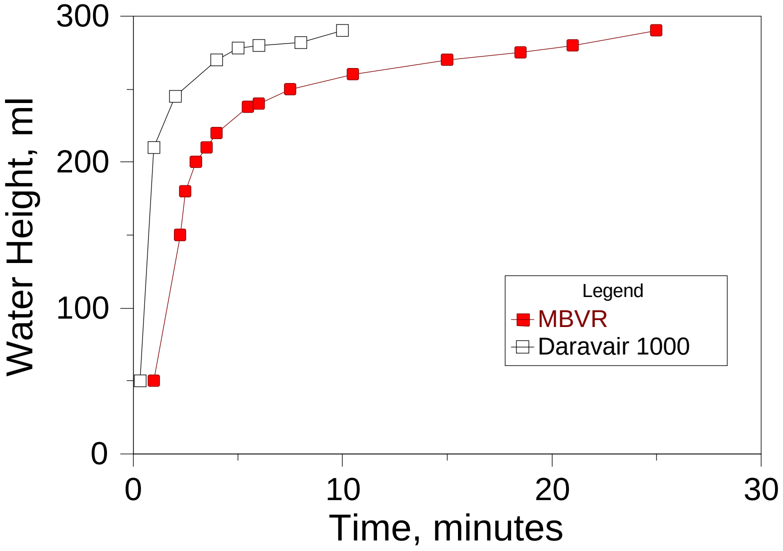


Figure 11. Comparison of MBVR and Daravair 1000 foam drainage in the absence of cement.

It can be seen in Figure 11 that, in both of these experiments, the ultimate foam drainage approaches 300 ml. However, the MBVR seems to have a short induction period before drainage begins and also may have an inflection point on the curve. This type of behavior is associated with foams having a homogeneous distribution of liquid phase. In this case it takes a few minutes for enough liquid to drain into the borders to cause sufficient pressure for the liquid to begin to drain out of the foam. The flow from the foam formed by Daravair 1000 begins immediately as the liquid is released immediately. Table 8 shows the comparison of the drainage data for the air entraining admixtures used in this work. From Table 8, the following points can be made. First, the V_0 values are approximately constant and are not different at the 95 % confidence level. Second, the rate of drainage (-k) is about 3 times slower for vinsol resin based admixtures (MBVR, MBVRLS, Adair 1800) than for the other admixtures except for Darex II. Heating of the water had little effect on the behavior of Daravair 1000, but using distilled water

had a marked effect on Daravair 1000. When distilled water was used for the test, Daravair 1000 acted like the vinsol resin based admixtures. This is probably due to the precipitation of Daravair 1000 with the cations present in tap water. Distilled water had no effect on MBVR at the 95 %

confidence level. The values for the %drain are similar to those found by Gutmann using the

Table 8. Drainage Data for the Admixtures Used in this Work

Admixture	V_0	-1/k	r^2	%drain	%wif
Daravair 1000	293.5	88.8	.980	2.2	6.1
MBVR	280.1	242.2	.942	6.6	6.2
MBVRLS	292.2	311.3	.926	2.9	-
D1000 Dist.	321.7	304.3	.905	-	-
MBVR Dist.	263.4	145.2	.773	12.2	-
D1000 Hot	288.3	54.7	.727	3.9	-
Daravair 1400	271.3	95.4	.972	9.6	16.1
Adair 1800	302.8	372.8	.957	-	-
Darex II	309.4	375.4	.904	-	-
Conchem Air	285.5	107.3	.980	4.8	10.0
MBAE 90	286.1	109.4	.980	4.6	18.8

same foam test (although the type of blender may make a difference). Gutmann found that 98.1 % of the foam from a wood resin salt (a vinsol resin) drained in 1 hour. This would be 1.9 %drain in Table 6, which compares reasonably well with the data given above. In general the %drain is not too different for any of the admixtures for which it can be calculated and is between 5 and 10 % with the final foam being about 10-20 % water.

Foam Drainage with Cement

Cement 2 While the data found in the absence of cement is interesting, far more important is the data found when cement is present in the foam test. As this turns the foam into a three-phase system rather than a two-phase system, it is expected that the presence of the third phase (solid cement) will have a great effect on the foam drainage behavior. The cement particles will be carried into the foam, and they will collect primarily in the borders at which 3 bubbles meet not in the films between 2 bubbles. This will cause a decrease in the flow rate from the borders. The solid phase will also adsorb some of the admixture in solution, which can cause an increase in surface tension and will cause an increase in the drainage rate. When the admixture concentration in solution is low, the change in surface tension will dominate; while at high admixture concentrations, the amount of admixture adsorbed is negligible compared to the total admixture concentration and the drainage rate will decrease due to the blocking of the borders. It is expected that with the amount of admixture used in this work, the primary effect will be to lower the drainage rate. Figure 12 shows typical drainage curves found in this work. Comparison of Figures 11 and 12 show that the main difference for Daravair 1000 is that the final amount of water drained appears to be slightly less but the drainage time was approximately the same. For the MBVR, the amount of water drained at the end of drainage was much less than when no cement was present and the time to reach the final amount drained was longer. This will be much easier to see by tabulating the data. Figures 13-14 show a comparison of the

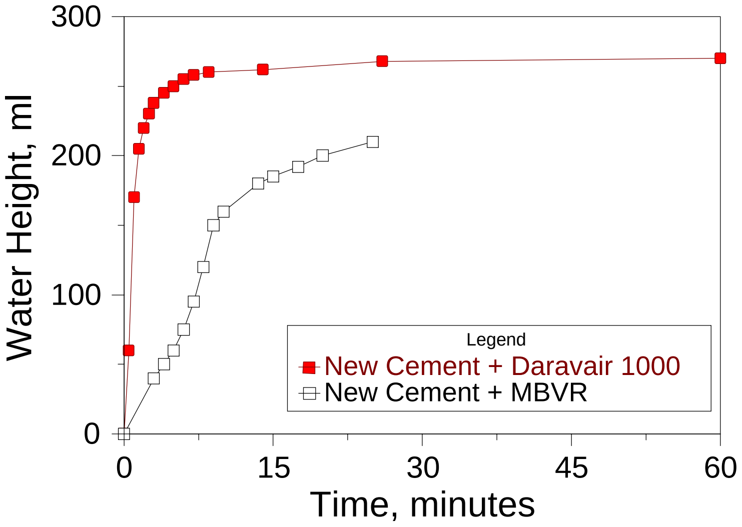
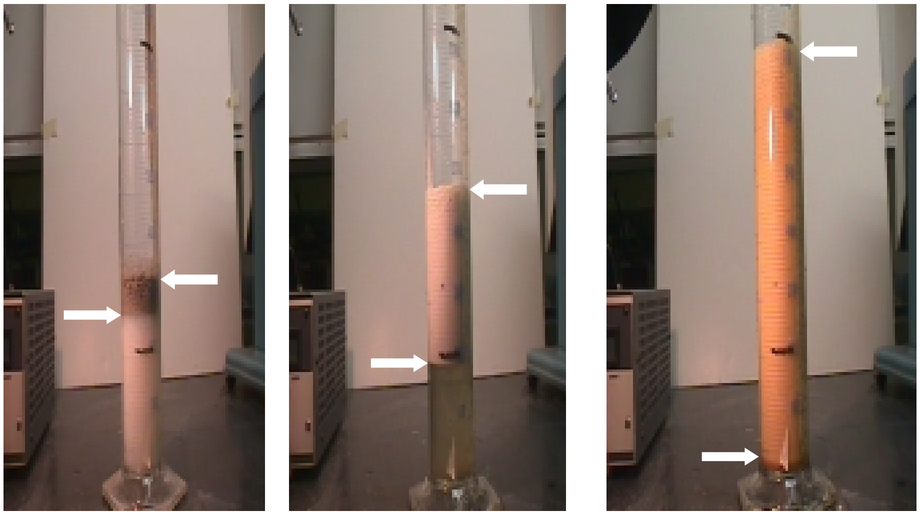


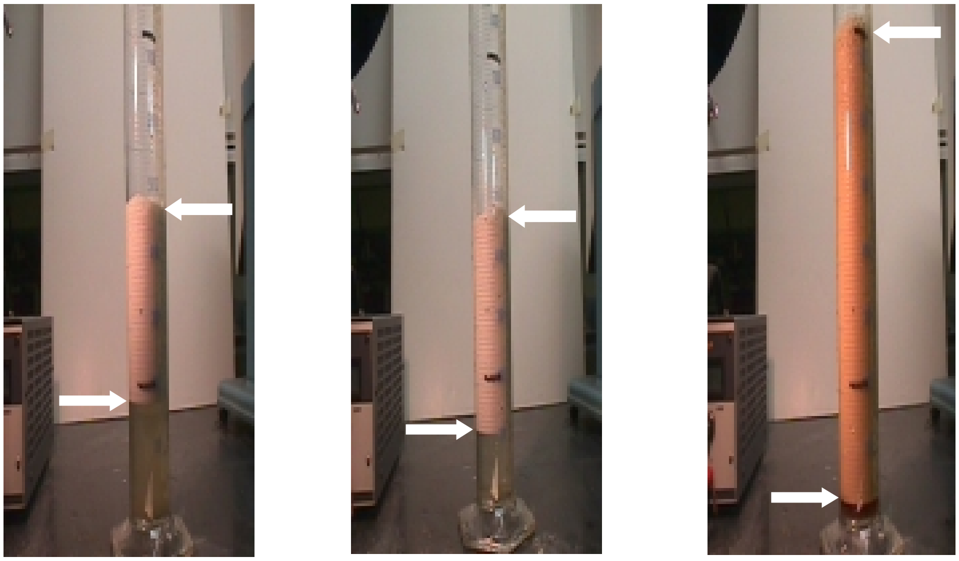
Figure 12. Typical foam drainage curves for Daravair 1000 and MBVR with Cement 2.

amount of water drained from the foam for the six admixtures used after 1 minute of drainage. Table 9 contains the data for the cement 2 with the various air entraining admixtures. Comparing this table to Table 8, it can be seen that the V_0 values have dropped significantly for all the admixtures except for Darex II, while the rates have dropped or stayed constant for all the admixtures except for MBVR for which it increased. The Adair 1800 exhibited some anomalous behavior as the drainage for this admixture began fairly rapidly, then dropped essentially to zero from about 3 to 6 minutes, then began to drain again. Also, during the time no drainage occurred, black dendrites were seen to leave the foam and go into the water phase. These dendrites were probably cement particles that had been lifted into the foam and then were either washed out or they fell out as the air bubbles that brought them into the foam burst or coalesced. This behavior caused the abnormally low correlation coefficient of 0.692. Thus, the presence of the cement particles decreases the amount of water drained from the foam from 90-95 % to 75-85 % for Conchem, MBAE 90, Daravair 1400 and Daravair 1000. For MBVR and Adair 1800, the amount of water held in the foam decreases from about 95 % to about 50-55 %. In addition the water in foam goes from 5-10 % up to about 20 % for most of the admixtures and over 30 % for MBVR, Adair 1800 and Daravair 1400. The rates of drainage have not changed much except for MBVR which drains much slower and Darex II which drains much faster. Darex II when combined with cement immediately forms a very low water foam so that only about 20 ml of water drains from the foam after the foam is poured into the graduated cylinder. 260 ml of water does not even enter the foam when cement is present.



Darex II Conchem Air MBVR

Figure 13. Comparison of foam drainage after 1 minute for Darex II, Conchem Air and MBVR. Right pointed arrows indicate the foam/water line; left pointed arrows indicate the top of the foam.



MBAE 90 Daravair 1400 Adair 1800

Figure 14. Comparison of foam drainage after 1 minute for MBAE 90, Darvair 1400 and Adair 1800. Right pointed arrows indicate the foam/water line; left pointed arrows indicate the top of the foam.

Table 9. Foam Drainage Parameters for Admixtures with Cement 2

Admixture	V_0	-1/k	r^2	%drain	%wif
Conchem Air	257.2	88.3	.994	14.3	23.4
MBAE 90	259.9	89.8	.999	13.4	21.1
Adair 1800	138.2	79.7	.692	53.9	31.6
Daravair 1400	223.8	148.4	.990	25.4	35.2
Darex II	283.6	7.48	.970	5.5	19.0
Daravair 1000	261.3	93.0	.989	12.9	20.5
MBVR	162.9	376.4	.938	45.7	28.1

Cement 1 Table 10 contains the drainage data when cement 1 was used. The only statistically significant difference is between Daravair 1400 which has more water drain from it than drained with cement 2. The difference between the vinsol resin based and the synthetic admixtures is readily apparent in this table. The vinsol resins keep more water in the foam, while draining much more slowly. This can be attributed to the cement particles blocking the 3 bubble borders and the fact that little of the action of vinsol resin changes due to adsorption. This seems to indicate that the vinsol resin does not adsorb onto the cement or at the air/water interface. This will be confirmed in the analytical techniques section. For the synthetic admixtures, the adsorption of the admixture seems to balance the presence of the cement in the foam borders. The effect of adsorption of these admixtures will also be seen in the analytical techniques section.

Table 10. Foam Drainage Parameters for Admixtures with Cement 1

Admixture	V_0	-1/k	r^2	%drain	%wif
Conchem Air	263.3	98.3	.977	12.2	16.6
MBAE 90	254.4	93.1	.999	15.2	23.3
Adair 1800	153.0	74.5	.783	49.0	29.6
Daravair 1400	240.4	139.4	.987	19.9	28.4
Darex II	282.0	5.7	.967	6.0	23.1
Daravair 1000	264.0	100.1	.996	12.0	20.5
MBVR	185.0	399.9	.965	38.3	25.8

Alkali Sulfates The effect of added alkali sulfates was examined by adding 1 % alkali (either potassium or sodium) sulfate to cement 2 and determining the effect on foam drainage. The alkali sulfates were added to simulate the difference between the cements 1 and 2 found during petrography. Table 11 shows these results for sodium sulfate, while Table 12 shows the results for potassium sulfate. The addition of alkali sulfate does change the foam drainage behavior of Daravair 1400 from the behavior of the cement 2 to that of the cement 1, but has little effect on the other air entraining admixtures.

Table 11. Foam Drainage Parameters for Admixtures with Cement 2 with Sodium Sulfate

Admixture	V_0	-1/k	r^2	%drain	%wif
Conchem Air	257.4	87.1	.945	14.2	-
MBAE 90	260.7	84.6	.958	13.1	21.6
Adair 1800	169.5	116.6	.724	43.5	33.5
Daravair 1400	243.3	129.8	.982	18.9	29.2
Darex II	281.3	25.4	.887	6.2	19.4
Daravair 1000	263.0	97.6	.995	12.2	21.0
MBVR	159.4	353.0	.934	46.9	29.1

Table 12. Foam Drainage Parameters for Admixtures with Cement 2 with Potassium Sulfate

Admixture	V_0	-1/k	r^2	%drain	%wif
Conchem Air	262.5	86.6	.956	12.5	22.1
MBAE 90	263.7	90.5	.932	12.1	-
Adair 1800	166.6	155.6	.712	44.5	32.1
Daravair 1400	242.6	129.4	.986	19.1	29.8
Darex II	281.3	25.4	.887	6.2	19.4
Daravair 1000	265.2	101.5	.997	11.6	-
MBVR	169.1	466.4	.969	43.6	28.0

Hot Cement and Added Aggregate Heating the cement produced similar results to unheated cement. However, these tests were run under a different test procedure in which the cement was added to the water before the admixture was added. This procedure caused a completely different type of behavior from MBVR which showed four distinct regions: a black, particle-heavy region at the bottom of the foam, a lighter foam, a dry foam on top with the fourth layer the water layer.

Addition of 1 gram of powdered quartzite had little effect on the foam test for MBVR and Daravair 1000 which were the only admixtures for which this test was run. For MBVR, $V_0 =$ 175.7 and –(1/k) = 355.9 and the correlation coefficient was 0.977. For Daravair 1000, $V_0 =$ 258.5 and –(1/k) = 107.5 and the correlation coefficient was 0.999. These values can be seen to be essentially equal to the values in Table 9-12.

Tests with Job Cements Foam drainage tests were also performed with four cements from jobs around the state. These cements were used on jobs whose time of use ranged from September 30, 1996 to April 14, 1998. These cement samples therefore span the range of time from few failing concrete strength tests to many failing concrete strength tests. Table 13-16 shows the values for V_0, -1/k and r^2 for these cements. Comparison of these tables with the previous tables shows that once again there is very little difference in the foam test for different cements, and that the differences between the action of the various admixtures is very consistent.

Table 13. Foam Drainage Test Parameters for P3115(3) 81 3953 – 9/30/96

Admixture	V_0	-1/k	r^2	%drain
Darex II	285.6	11.4	.839	4.8
Daravair 1400	230.5	118.6	.750	23.2
Adair 1800	138.1	386.2	.982	54.0

Table 14. Foam Drainage Test Parameters for BRO 8049 (9) – 5/97

Admixture	V_0	-1/k	r^2	%drain
Darex II	282.1	12.3	.856	6.0
Daravair 1400	227.8	100.0	.734	24.0
Adair 1800	163.4	589.4	.980	45.5

Table 15. Foam Drainage Test Parameters for PH0115 (33) 82 – 8/7/97

Admixture	V_0	-1/k	r^2	%drain
Darex II	286.0	4.24	.941	4.7
Daravair 1400	222.0	98.1	.819	26.0
Adair 1800	172.0	768.9	.973	42.7

Table 16. Foam Drainage Test Parameters for BRO 8050 (45) 50 – 4/14/98

Admixture	V_0	-1/k	r^2	%drain
Darex II	279.5	7.37	.797	6.8
Daravair 1400	231.6	101.4	.734	22.8
Adair 1800	156.3	869.9	.989	47.9

Foam Structure The structure of the foams from the various air entraining admixtures was examined by placing a small sample of the foam between two glass microscope slides and viewing the bubbles and particles in the foam through an optical microscope. Figures 15-19 show the foam structure for Adair 1800, Daravair 1400, MBVR, Conchem Air and MBAE 90. These images were taken at 500x magnification. The primary difference between these foams seems to be that the bubble wall thickness is greater (perhaps as much as twice as great) for the vinsol resin based admixtures (MBVR, Adair 1800). It also appears, although this is much more difficult to substantiate, that the vinsol resin based admixtures have more cement particles on their bubble surfaces.

Adair 1800

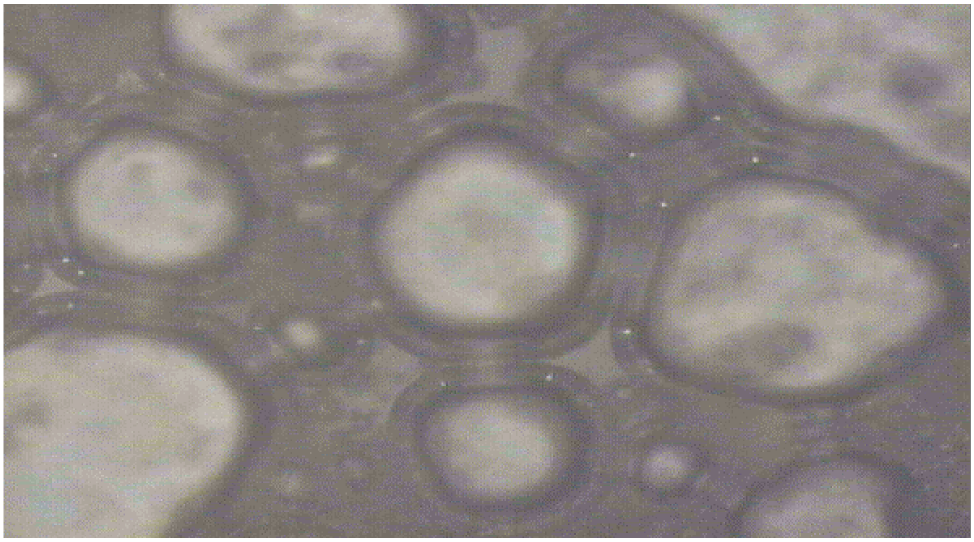


Figure 15. Foam from Adair 1800 foam test at 200x.

Daravair 1400

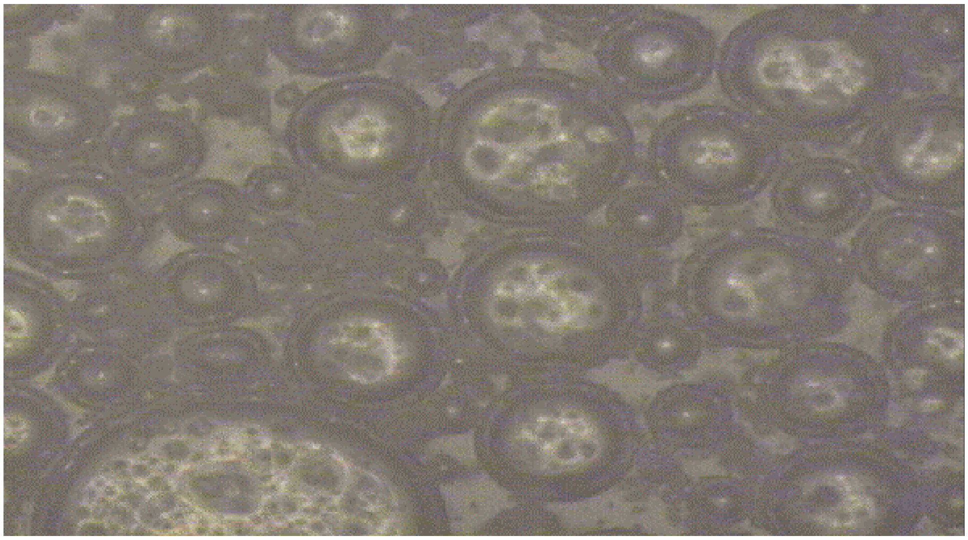


Figure 16. Foam from Daravair 1400 foam test at 200x.

MBVR

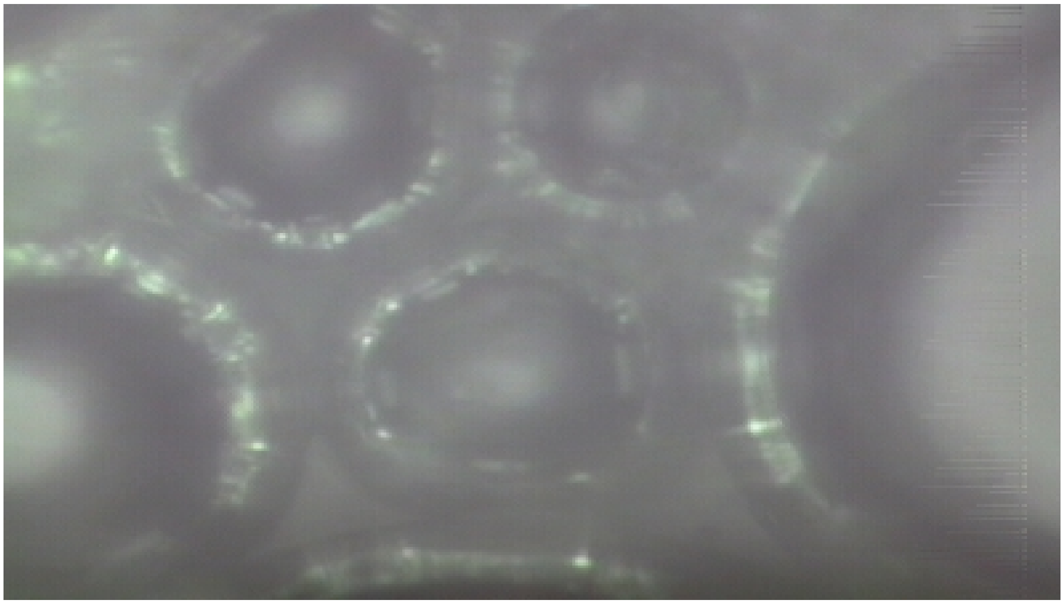


Figure 17. Foam from MBVR foam test at 500x.

Conchem Air

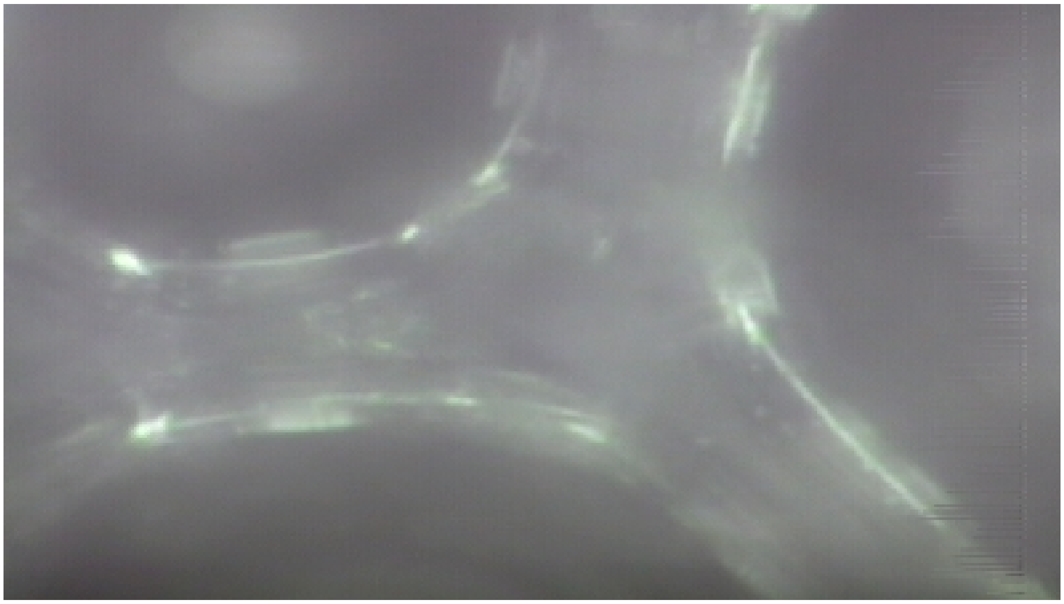


Figure 18. Foam from Conchem Air foam test at 500x.

MBAE90

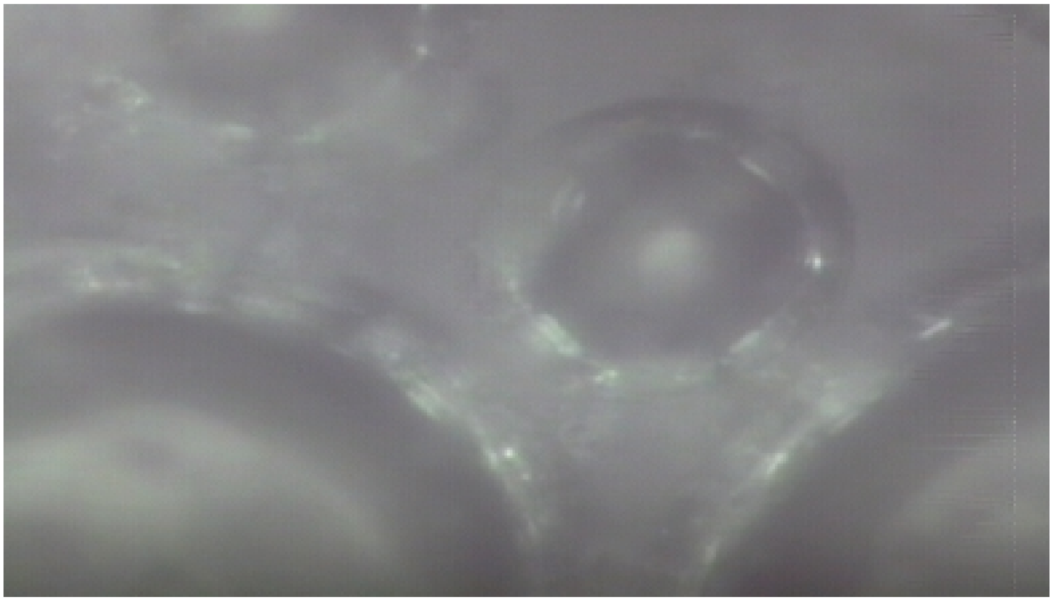


Figure 19. Foam from MBAE 90 foam test at 500x.

Mixing Admixtures   Several tests were conducted to determine the foam drainage characteristics of mixtures of vinsol resin with synthetic admixtures. Table 17 shows the results of mixing MBVR vinsol resin with Daravair 1000 and MBVR with MBAE 90. The results in this table indicate that mixes are 50:50 or greater in MBVR drain similar to MBVR, while mixes less than 50:50 drain similar to the synthetic admixture.

Table 17. Foam Drainage Parameters for Mixed Admixture Systems with Cement 2

	Ratio of MBVR:Synthetic									
Synthetic Admixture	0:100		20:80		50:50		80:20		100:0	
	V_0	-1/k	V_0	-1/k	V_0	-1/k	V_0	-1/k	V_0	-1/k
Daravair 1000	261.3	93.0	230.9	129.8	163.8	391.0	172.0	401.9	162.9	376.4
MBAE 90	259.9	89.8	242.2	107.6	167.9	328.3	160.9	405.7	162.9	376.4

Analytical Techniques

Microhardness

Purpose: Microhardness testing was performed to compare the mechanical properties of concrete matrix materials from representative cylinders. The measured microhardness is often directly proportional to strength. This test was performed to determine if the pastes were different in strength to correlate with structural changes seen in SEM analysis.

Method: The Vickers indentation microhardness of good and bad concrete samples was measured in the following manner. Several small samples from laboratory cylinders were collected. Samples from cylinders having a compressive strength of 4458 psi and 3663 psi were used. Samples with a relatively flat side and no obvious aggregate at the surface were chosen and placed flat side down in a die and surrounded by diallyl phthalate mounting compound. After approximately eight minutes of heating the mount was completed and the heat removed. The concrete in the mount was polished with 400 and then 600 grit silica carbide sand paper on a rotary wheel. Polishing was necessary to provide a smooth surface for indentation. One difference between the samples was evident during polishing. The weaker concrete came off the surface in chunks, while the stronger surface polished easily. The result of polishing can be seen in Figure 20. The polished samples were then placed in a Buehler Micromet 4 microhardness tester. A 300 gram load was used along with 13 second dwell time. The microhardness was found by measuring the size of the impression left by the square-based pyramid shaped Vickers indenter. The software of the Micromet 4 calculated the diagonal length of the diamond shaped impression and from the two diagonal lengths the Vickers microhardness was determined.

Results: Table 18 shows the results from these experiments. It can be seen that the samples from the better cylinders have significantly higher microhardness than the samples from the weaker cylinder. Typical values for non-air entrained cement pastes are 50-60 kg/mm^2 [5]. This result indicates that the paste formed in the weaker cylinder was significantly worse in terms of its strength (microhardness is often directly proportional to strength) than the paste from the stronger sample.

Figure 20. Polished surfaces of concrete microhardness samples.

Table 18. Comparison of Vickers Microhardness (300 gram load) for Concrete Samples

Sample Cylinder Compressive Strength	Vickers Microhardness (kg/mm^2)
4458	32.8±12.2
3699	11.5±6.4

Surface Tension

Purpose: The surface tension of water/admixture solutions with and without cement was measured to determine the effect of air/entraining admixture at the liquid/vapor interface. This interface is critical for producing the air-void system. The use of cement was necessary to simulate typical concrete pore solution and to account for the effect of air entraining admixture adsorption to the cement particles. This test assessed possible causes 1 (cement) and 4 (air entraining admixtures).

Method: The surface tension of the air entraining admixtures used in this work was measured on a Central Scientific CSC-DuNouy Interfacial Tensioniometer and a Kruss K10T digital tensiometer. Both of these use a DuNouy ring based system to measure the interfacial tension of liquids. In these experiments 10 drops (~0.5 ml) of admixture was added to 16 fl.oz. (473 ml). For the solution, distilled water was used as was a simulated concrete pore solution, which was made by adding 1 gram of cement to 16 fl.oz. of tap water. The pore solution was allowed to equilibrate for 1 hour before the admixture was introduced. After the addition of admixture, all solutions were allowed to equilibrate for 1 hour.

Results: The results of the surface tension measurements are shown in Table 19. Neither cement 2 or 1 had much of an effect on the surface tension behavior of Conchem Air, MBVR and Adair 1800. Darex II and Daravair 1400 were significantly effected by the presence of the cement particles but there was little difference between the behavior with the cements 1 and 2.

Table 19. Comparison of Surface Tension of Various Admixtures without Cement and with Both Cements 1 and 2

Admixture	Surface Tension, dyne/cm No Cement	Surface Tension, dyne/cm Cement 1	Surface Tension, dyne/cm Cement 2
None	67.0	57.0	63.4
Adair 1800	50.5	51.4	52.5
Darex II	39.4	50.2	50.0
Daravair 1400	45.0	49.0	49.5
MBVR	49.1	49.4	49.2
Conchem Air	46.3	47.0	46.5

Contact Angle

Purpose: Contact angle measurements were used to examine the adsorption of air entraining admixture to simulated aggregate surfaces and to determine whether aggregate hydrophobicity contributes to clustering of air voids in the vicinity of aggregate surfaces. This test assessed cement (cause 1) and air entraining admixtures (cause 4).

Method: The contact angle of water bubbles placed on treated glass slides was measured with a Rame-Hart model 100 contact angle goniometer. The glass slides were treated by placing the slides in a solution of air entraining admixture for one hour. The admixture solution was made by the same procedure as that used for preparing admixture solutions for surface tension measurements.

Results: The results of the contact angle work show that there no statistical difference between the contact angles of any of the admixtures when comparing cement 2 with cement 1. However, the tests with Darex II and Daravair 1400 showed significantly greater contact angles than Adair 1800 and MBVR. Conchem Air had an intermediate contact angle. Table 20 shows this data. These results correlate with the surface tension work, in that Darex II and Daravair 1400 gave differences between the cement and no cement indicating that the admixture had adsorbed onto the cement. This adsorption then leads to the increased contact angle. The Conchem Air, MBVR and Adair 1800 show little adsorption on the cements; thus, they exhibit smaller contact angles.

Table 20. Contact Angle of Air Entraining Admixtures with Cements 1 and 2

Admixture	Contact Angle with Cement 2	Contact Angle with Cement 1
Adair 1800	17.8 ±4.4	13.8 ±3.8
Darex II	26.5 ± 5.6	24.5 ± 2.2
Daravair 1400	29.2 ± 2.3	32.8 ± 5.0
MBVR	20.3 ± 0.8	19.8 ± 2.7
Conchem Air	23.0 ± 3.6	25.8 ± 6.0

Higher contact angle values indicate that the surface is more hydrophobic and therefore more likely to collect air bubbles at the solid surface. Thus, because the glass slide is very similar to quartzite aggregate in terms of its surface chemistry, air bubbles are more likely to congregate at the paste/aggregate interface for Darex II and Daravair 1400 than for Adair 1800 and MBVR. This may be contribute to the “floccing” of air bubbles at the paste/aggregate interface in low strength concretes.

X-Ray Diffraction

Purpose: X-ray diffraction was performed to measure the amounts of cement constituents

(C2S, C3S, etc.) in the materials used in this research. Because large differences were observed in some of the testing protocols, the nature of the initial materials was measured and compared. This technique tested the cement, possible cause 1.

Method: X-ray diffraction experiments were performed by the South Dakota School of Mines and Technology's Engineering and Mines Experiment Station (EMES). Samples of cement powder were mounted onto glass fiber filters using a Tubular Aerosol Suspension Chamber (TASC) developed by Dr. Briant Davis. The sample is drawn onto the filter by a controlled air flow that assures random orientation of the sample particles.

Sample scans were performed on a Philips X-Ray Diffractometer using Cu K_α radiation at a wavelength of 1.54178 Angstroms. A scan step of 0.02° 2θ and 2 second dwell time were used. In addition, a scan from 29° to 36° using a 4 second dwell time was performed to improve resolution of the cement peaks of interest in this range.

The integrated intensities for C2 (C_3S Tricalcium Silicate), C3 (C_3A Calcium Aluminate), and C4 (C_4AF Calcium Ferro-Aluminate) were obtained by hand triangle approximation because of the partially interfering peaks of all cement phases. The 4 second dwell scan was used for this calculation. The software-generated intensity for C1 (C_2S Dicalcium Silicate) was used in the analysis. The primary peaks for all cement components are not suitable for quantitative analysis due to multiple interferences. Lower intensity peaks were used at the following 2θ angles:

C1 34.50°, C2 30.13°, C3 33.17°, C4 33.75°

Results: The quantitative analyses were performed using the RIM (Reference Intensity Method [13]). All interferences from cement components and other minerals present were taken into account during this analysis. Table 21 shows the amounts of C3S, C2S, C3A, C4AF, calcite and gypsum found for the cements used in this work.

Table 21. Cement Constituents Present from X-ray Diffraction Data. All Data is Given in Weight Percent

Cement	C3S	C2S	C3A	C4AF	Gypsum
2	39.7	55.8	0.5	4.0	-
1	31.5	60.5	1.0	7.0	-
9-30-96	36.8	48.2	4.0	8.1	0.8
5-97	35.6	44.8	4.7	10.9	1.2
8-7-97	29.7	49.3	4.7	13.1	1.1
4-14-98	35.2	46.5	4.8	8.9	1.5

The primary difference between these cements by X-ray diffraction appears to be that cement 1 and the 8-7-97 cement have less C3S than the other cements. Also, the 1997 cements appear to have more C4AF. It should be noted that full quantitation of X-ray diffraction data for cement constituents is very difficult to perform accurately. However, as all the data was collected by the same operator and interpreted in the same manner, the data are at least relatively comparable.

The strength of concrete is primarily due to the C3S and C2S. C3S is responsible for the early time strength, while C2S contributes to the long term strength [14]. The data for C3A and C4AF are erratic. In general, they seem to increase early strength but moist storage may reduce long term strength [14]. In addition, C3A may have a synergistic effect with C3S on the strength [14]. Thus assuming good storage conditions, cement 1 should probably be stronger than cement 2 although in practice the opposite effect was found. Thus, either cement 1 was stored under moist conditions or the strength differences between the cements was due to something other than the primary constituents of the cement. For instance, alkali sulfate content has been shown to decrease the strength [14].

Soluble and Total Alkali Content

Purpose: As the alkali content, particularly soluble alkalies can have a large effect on the behavior of concrete systems, the total alkali and soluble alkali contents were measured. This investigation tested the cement, possible cause 1.

Method: The six cements utilized in this work were tested for their soluble and total alkali contents. These experiments were performed according to ASTM C114 [15] by the EMES of SDSM&T.

Results: Table 22 shows the results for the six cement samples used in this work. The primary differences between these cements seems to be that cement 1, which performed poorly in lab tests, contains a very high fraction of soluble alkalis despite the small difference in total alkali content. This seems to agree with the petrographic report detailed later in which cement 1 displayed more soluble alkali grains than cement 2. The only difference between the job cements is that the 5-97 cement had significantly more soluble alkalis than the other three job cements.

Table 22. Total and Soluble Alkali Contents of the Cement Samples Used in this Work. All data are given in Weight Percent Except for the % soluble (%sol.) Data

Cement	Soluble Na	Soluble K	Total Na	Total K	%sol. Na	%sol. K
2	0.026	0.35	0.085	0.48	30.6	72.9
1	0.027	0.40	0.073	0.42	37.0	95.2
9-30-96	0.020	0.29	0.092	0.43	21.7	67.4
5-97	0.022	0.33	0.073	0.38	30.1	86.8
8-7-97	0.021	0.36	0.100	0.51	21.0	70.6
4-14-98	0.017	0.21	0.079	0.34	21.5	61.8

Zeta Potential

Purpose: The charge behavior of the cement and aggregates was measured through the determination of the zeta potential. These measurements were performed to assess whether any material was present at the surface that effect the charge behavior. The charge behavior is also important in the formation of the air-void system as the cement particles help stabilize the air bubbles within the concrete. This test examined possible cause 1 (cement) and possible cause 2 (dirty rock).

Method: The zeta potential of the aggregates and cements 1 and 2 were measured utilizing a Malvern Instruments Zeta Sizer 4 at the University of Utah. The materials were tested by making a dilute solution of particles in a 0.001 M KCl solution. The dilute solution was then injected into the machine. The particles injected interact with two laser beams which cross. The particles are subject to an electric field and the change in the interference of the laser beams yields the electrophoretic mobility and hence the zeta potential.

Results: For the aggregates, the dolomite aggregate was positively charged at all pH values tested (pH 6-11.5). This is as expected as the point of zero charge for dolomite is usually given as ~12.5 [15]. When tested at pH 4.7 the charge was found to be nearly zero probably due to dissolution of some of the dolomite, giving a much higher concentration of gangue silica in the tested material. Quartzite aggregate was also tested and the aggregate was found to be negatively charged at all pH values tested (pH>2.5). This once again agrees with the literature as the point of zero charge of silica is usually given as pH ~1.8 [16].

For the cements tested (cements 1 and 2), the zeta potential was found to be essentially zero. Cement 1 had a zeta potential of +0.90 with a half width of 2.17 mV, while cement 2 had a zeta potential of +1.42 with a half width of 2.31. These samples were tested at the natural pH of the slurry, about pH 8.5. The zeta potential does agree generally with the literature values for cement which state that most cements are slightly positively charged.

Fourier Transform Infrared Analysis

Purpose: Fourier transform infrared analysis (FT-IR) of the cements and air-entraining admixtures used in this work was performed to asses the differences between the materials in terms of their molecular bonding. This technique examined the cement (possible cause 1) and the air entraining admixtures (possible cause 4).

Method: The admixtures and cement 1 and 2 samples were examined by FT-IR. The admixtures were analyzed by performing liquid transmission experiments through thin (~10-15 mm) liquid layers. The water was subtracted from the spectrum and the resulting spectrum analyzed. The two cement samples were tested by diffuse reflectance measurements. The cement samples were ratioed against KBr and the resultant spectrum was analyzed.

Results: Figure 21 show the FT-IR spectra of the cements. The primary differences between the cement samples occur at 3639 cm^{-1} where the cement 2 has a very sharp band due to water bound to one of the silicate minerals; 3400 cm^{-1} where cement 1 has a sharper water band than the cement 2; and at ~2900 cm^{-1} where cement 2 exhibits a large band of unknown origin. The liquid transmission spectra of the admixtures were all difficult to interpret due to differences in the state of water as free water and the water in the admixtures. This limited the utility of examining the resultant spectra. It was seen that the Conchem air had considerable aliphatic character, and many of the admixtures exhibited a band at ~1568 cm^{-1} which is attributable to sodium carboxylate salts.

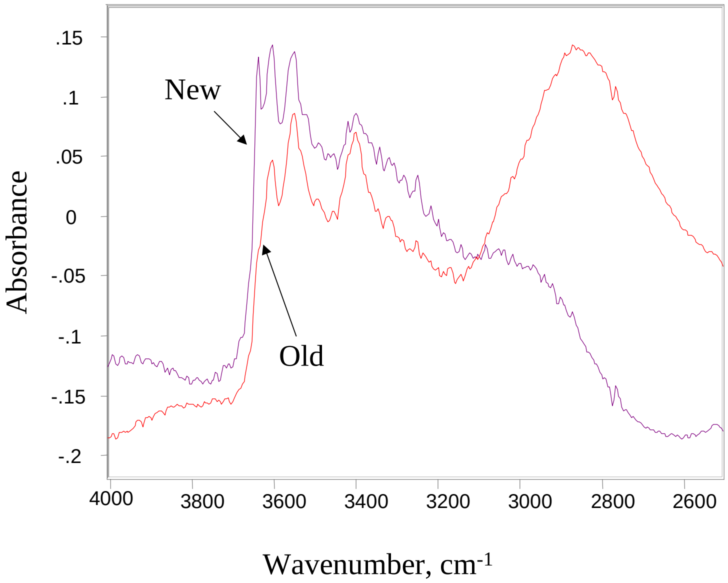


Figure 21. Fourier transform infrared spectra of cements 1 and 2.

Scanning Electron Microscopy (SEM)

Purpose: The purpose of the SEM examination was to determine if there are microstructural or microchemical characteristics of concrete specimens that might correlate with low compressive strength and with the use of particular starting materials or mixing practices. Specific microstructural features that were considered included overall air content, air void size, air void distribution, and paste density and porosity. Microchemical characteristics that were considered included examining the paste-aggregate transition zone for anomalous concentrations of ettringite, gypsum, or alkali sulfates.

Method: Three different types of material were examined by SEM: concrete laboratory cylinders, concrete pavement cores, and unhydrated cement powder. Samples of cylinders and cores were examined both as unpolished fragments of broken material and as polished thin sections. Cement powders were encapsulated in epoxy resin and prepared as polished thin sections.

Prior to examination, fragments or thin sections were coated with gold or carbon to eliminate surface charging in the SEM. SEM analyses were carried out in the Engineering and Mining Experiment Station at SDSM&T using a JEOL 840A SEM. SEM acceleration voltage was between 15-25 keV. Micrographs were acquired in both secondary and backscattered electron modes, and X-ray microanalyses were acquired with an energy-dispersive X-ray detector (EDX).

Results: Air Voids at the Interface between Cement Paste and Aggregate

General

Preliminary SEM examination of low-strength concrete cores (Sept. 29, 1997, see Figures 1 and 2) indicated two distinctive characteristics of the air void distribution that could contribute to low compressive strength. 1) Anomalously high concentrations of air voids were exposed on the surfaces of coarse aggregate particles around which failure had occurred. These air voids were bisected by the plane of failure, and corresponding air void concentrations (mirror images) were observed on the surfaces of the molds in the paste where the aggregate particle had been removed. 2) Air voids on these surfaces were not uniformly distributed but tended to occur in clusters or flocs, apparently held in mutual contact by surface tension forces. The air void clusters were observed both on limestone and quartzite aggregate surfaces.

Sample Selection and Preparation

In order to validate the initial findings, additional SEM observations were carried out on aggregate and paste mold surfaces. Specimens included both laboratory cylinders and pavement cores and were selected to cover a range of compressive strengths (3520-4622 psi).

Selection and preparation the specimens for this part of the study proceeded as follows. If the core or cylinder was not received in a fractured state, it was broken with a sledge hammer. A qualitative description of the resistance to fracturing was noted. The concrete was broken until there were enough small fragments (0.5-2.0 in.) to place in the SEM. Depending on the strength of the concrete, this required as few as 10 "hits" or as many as 30 "hits." A qualitative description of the mode of failure was also noted, particularly the proportion of aggregate pieces that failed through the particle as compared with those that failed at the interface around the particle. For example, in more resilient concrete (e.g., 4662 psi) it was estimated that fewer than one half of the aggregate failed around the particle, whereas in weaker specimens (e.g., 3660 psi) it was estimated that more than three fourths failed around the aggregate.

In an attempt to quantify the relative degree of debonding at the paste-aggregate surface, between 120 and 220 aggregates were counted on selected cylinders and cores. Those represented by a cast or mold surface were concluded to have broken around the aggregate and were thus debonded. Those represented by a fractured aggregate surface were concluded to have broken through the aggregate and the bonding was intact. The results of the counts are shown in Figure 22. There is a high correlation between aggregate debonding and low compressive strength. Specimens with compressive strengths below 3600 psi show debonding at more than 75 percent of the interfaces. In contrast, specimens with compressive strengths greater than 4400 psi show debonding at fewer than 55 percent of the interfaces.

In the next stage of the selection process, free pieces of aggregate or paste molds were examined at low magnification using a binocular microscope. Special attention was given to the presence of bisected air voids on these surfaces. Although some aggregate surfaces exposed the actual rock (limestone or quartzite), this was very rare; most surfaces had a very thin layer of paste (<0.5 mm or 500 μm) adhering to them. Qualitative notes on the number of exposed air voids on these surfaces were recorded. For example, in some relatively high strength (e.g., 4622 psi) concrete samples, air voids were virtually non-existent on aggregate surfaces, whereas in some relatively low strength (e.g., 3520 psi) samples air voids were evident or common on virtually every piece of aggregate examined. Typically 20-30 pieces of aggregate and/or paste molds were examined and 5-10 pieces showing the maximum concentration of air voids were selected for further examination in the SEM.

Results: SEM Observations

Figure 23 illustrates differences in air void concentration on aggregate surfaces observed in this study. Both aggregates are quartzite and both SEM micrographs were acquired at the same magnification (100X). Figure 23A shows a rare low-concentration cluster of air on an aggregate surface from a moderately high-strength laboratory cylinder (4622 psi). The overall concentration of air voids is low, and there is no tendency for flocculation. In contrast, Figure 23B shows a typical cluster of air voids from a low-strength laboratory cylinder (3663 psi). The overall concentration of air is anomalously high, air void diameters are generally large, and many air voids are flocced so as to share bubble walls with one or more adjacent air voids.

Concrete containing both quartzite and limestone aggregate was examined, although quartzite was much more common in this study (e.g., quartzite was used in all laboratory cylinders). No major differences in air void distribution or character were evident between limestone and quartzite specimens. Figures 24 and 25 compare SEM micrographs of quartzite and limestone aggregate surfaces from low strength specimens. Both types of aggregate show anomalously high concentrations of air voids and evidence for clustering or floccing. As noted previously, the typical mode of failure of the specimens was around aggregate, exposing the interfacial zone in plan view. However, in parts of some specimens the mode of failure made it possible to examine the aggregate-paste interface in a cross-sectional view. Figure 26 compares cross-sectional views of the interfacial zone adjacent to limestone (Fig. 26A) and quartzite (Fig. 26B). Both micrographs show a planar concentration of air voids within 0.5 mm (500 μm) of the aggregate. In general, a thickness of 100-400 μm seems to typify the transition from aggregate through the zone of clustered air voids to normal cement paste. Figure 27 goes on to illustrate incipient failure in the interfacial zone, with the plane of failure clearly bisecting the zone of air voids that are concentrated along the interface. The microstructure of cement paste in many low-strength specimens was distinctively open and porous. Figure 28 illustrates an air void cluster on the surface of quartzite aggregate. In Figure 28A it is clear that the air voids are close-packed or flocced. Bubble wall thicknesses are less than 10 μm at points of contact between adjacent air voids. Figure 28B shows the paste microstructure in a portion of the wall separating adjacent air voids. The paste is porous and contains abundant ettringite needles.

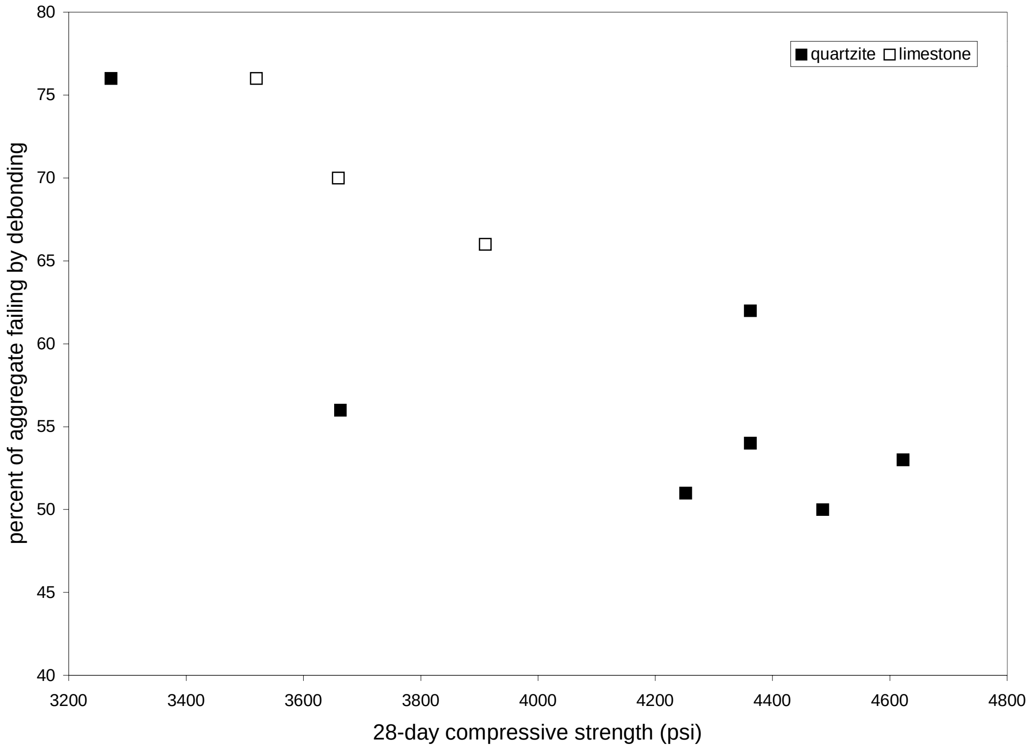


Figure 22. Comparison of compressive strength of concrete specimens with mode of failure at aggregate-paste bond. Vertical axis shows estimated percentage of aggregate that debonded from paste (failure around rather than through aggregate).

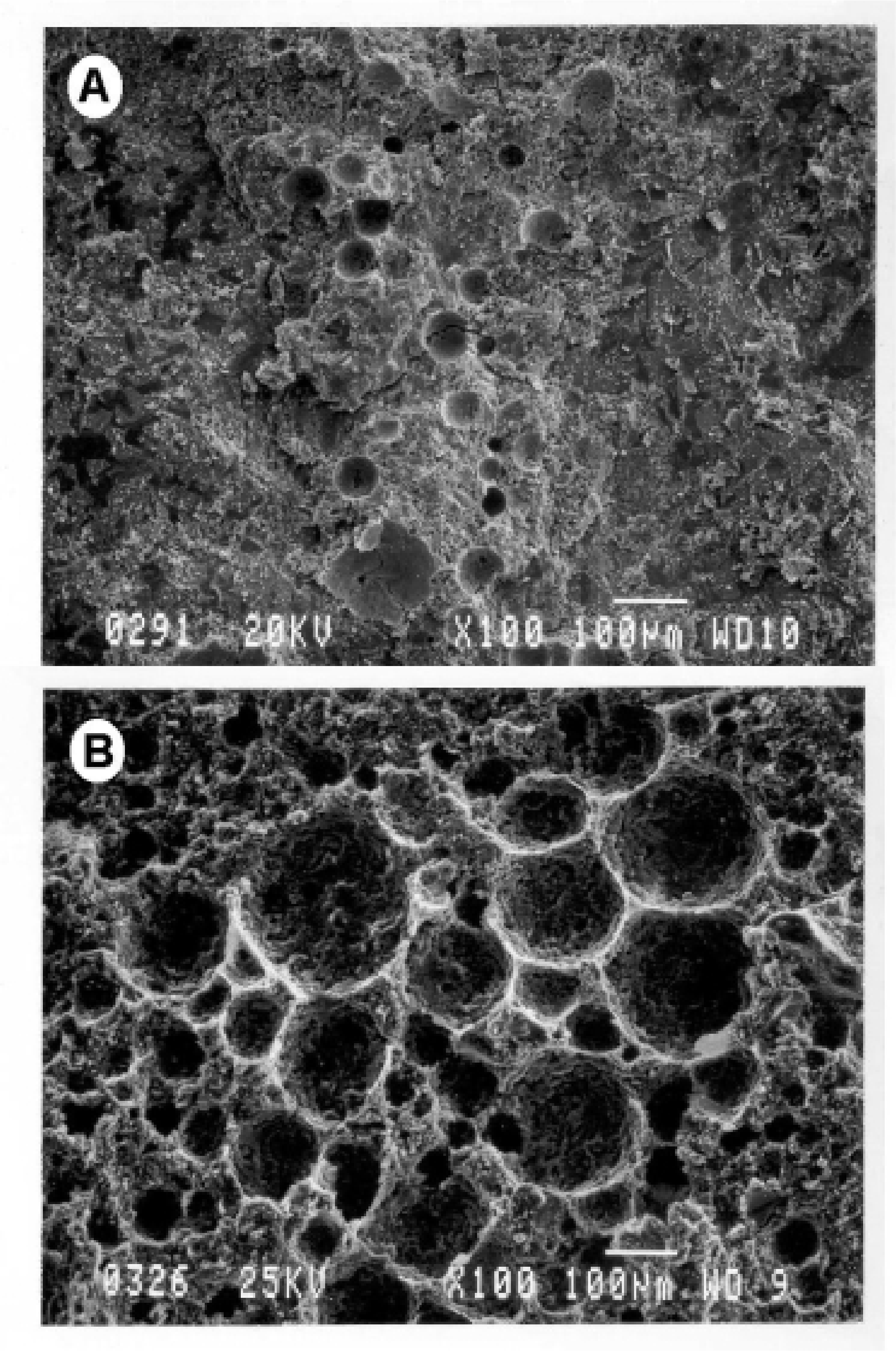


Figure 23. SEM micrographs of air voids at the interface between quartzite aggregate and cement paste. A. Relatively high strength sample (4622 psi). B. Relatively low strength sample (3663 psi). Bar scale is 100 µm.

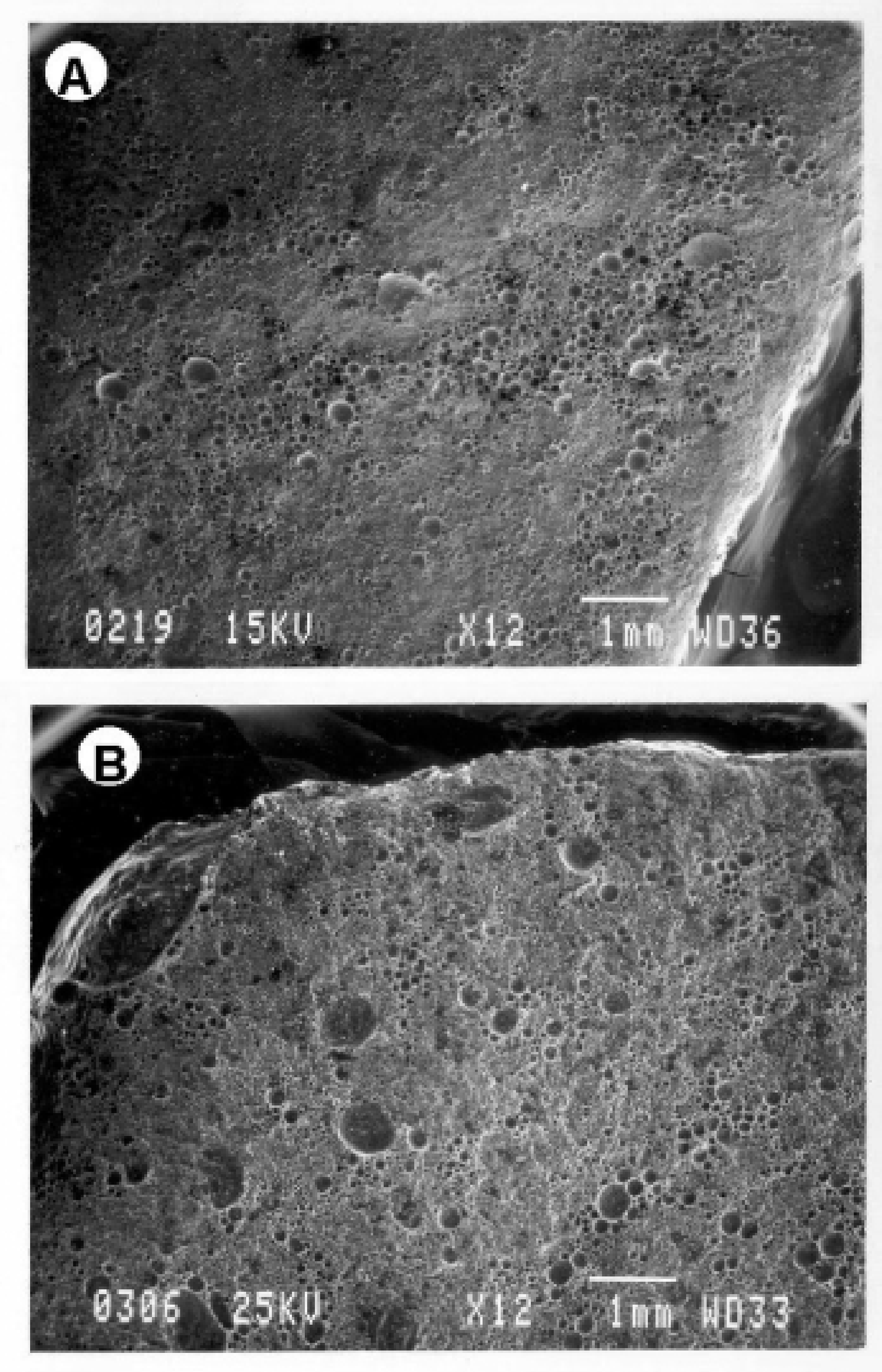


Figure 24. Low magnification SEM micrographs of low strength specimens, showing surface of aggregate where it debonded from cement paste. A. Limestone aggregate (3520 psi). B. Quartzite aggregate (3663 psi). Some large, irregular entrapped air voids (0.5-1.0 mm) are visible in addition to abundant entrained air. Bar scale is 1 mm.

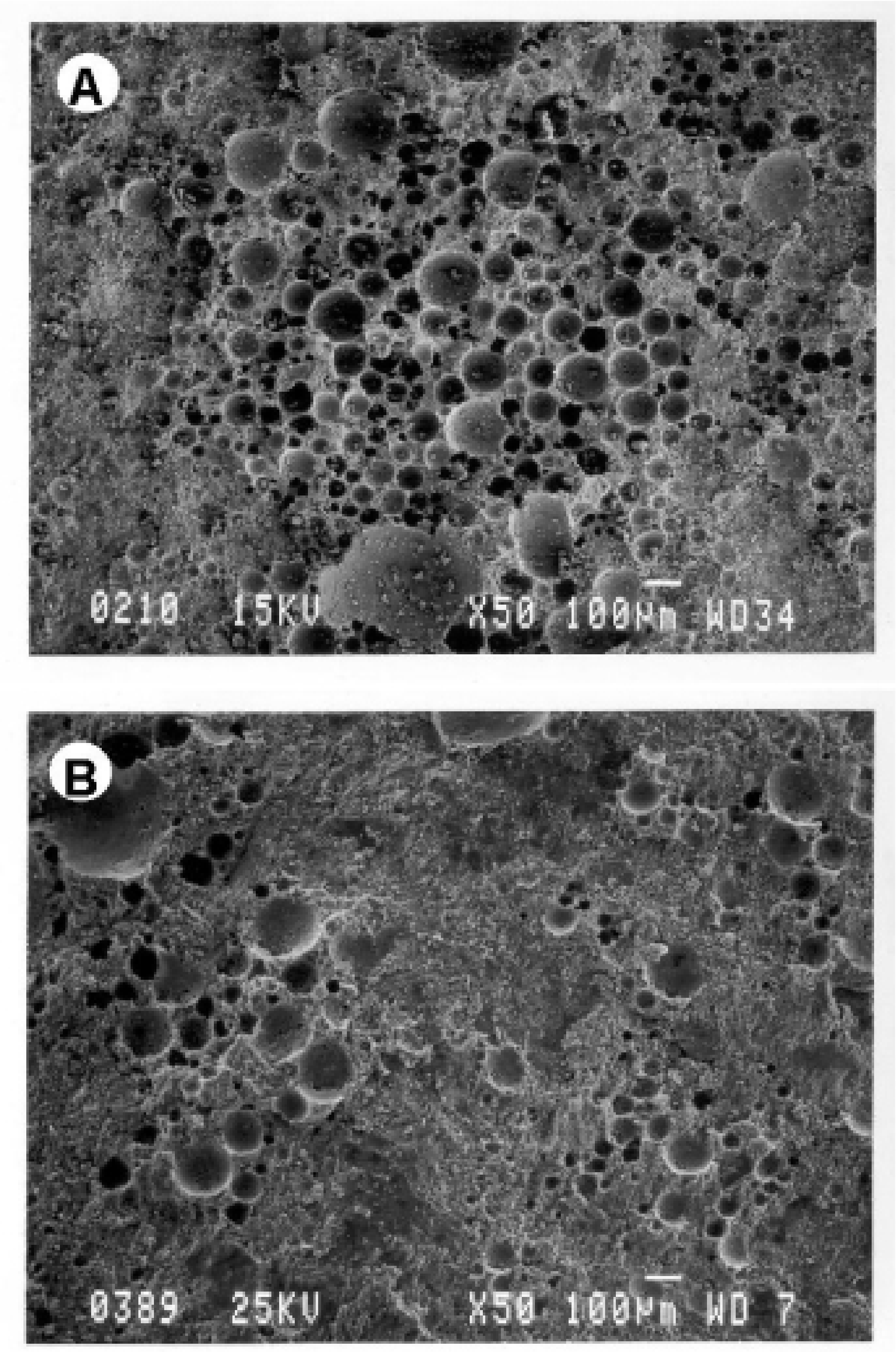


Figure 25. Medium magnification SEM micrographs of low strength specimens, showing surface of aggregate where it debonded from cement paste. A. Limestone aggregate (3520 psi). B. Quartzite aggregate (3272 psi at 14 days). Bar scale is 100 m.

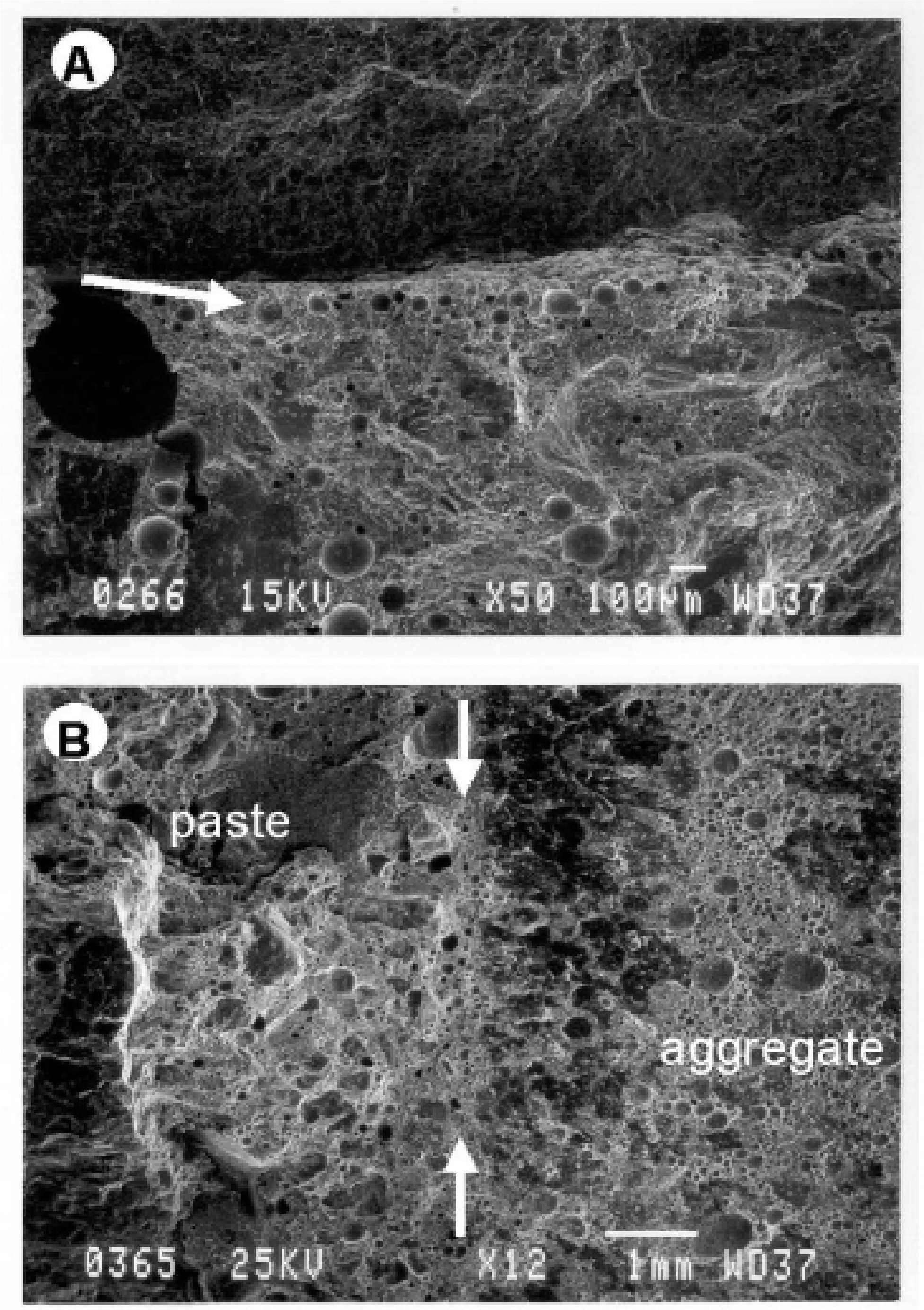


Figure 26. SEM micrographs of low-strength specimens showing aggregate-paste interface in cross section. Arrows point to air voids along interface. A. Limestone aggregate (3660 psi). B. Quartzite aggregate (3663 psi). Transition zone between aggregate and paste is 100-400 μm. Bar scale is 100 μm in A and 1 mm in B.

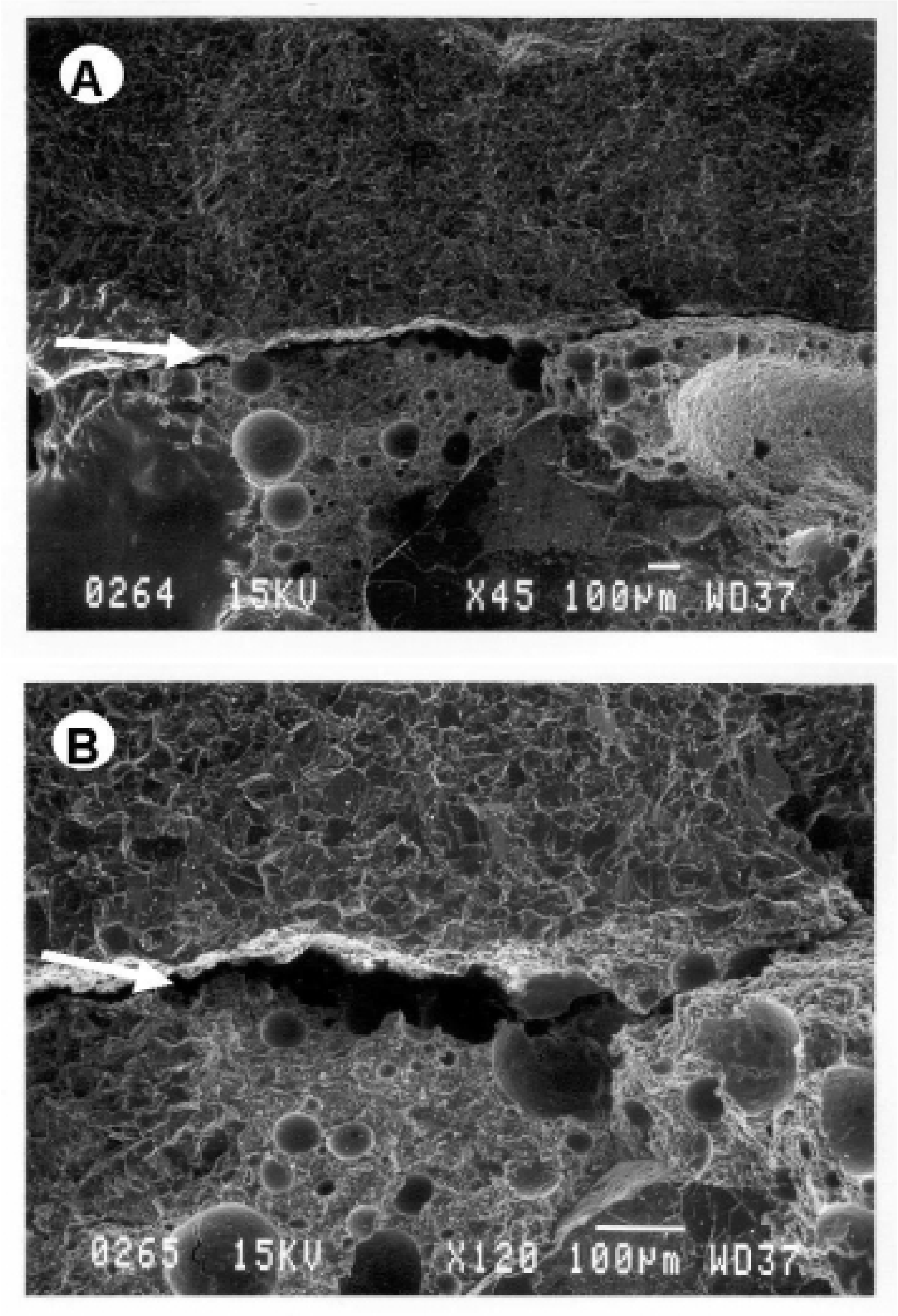


Figure 27. SEM micrographs of low strength specimen showing incipient failure at interface between cement paste and limestone aggregate. Fracture (arrows) follows interface and bisects air voids aligned parallel to the aggregate surface. Same specimen as Fig. 26A. Bar scale is 100 m.

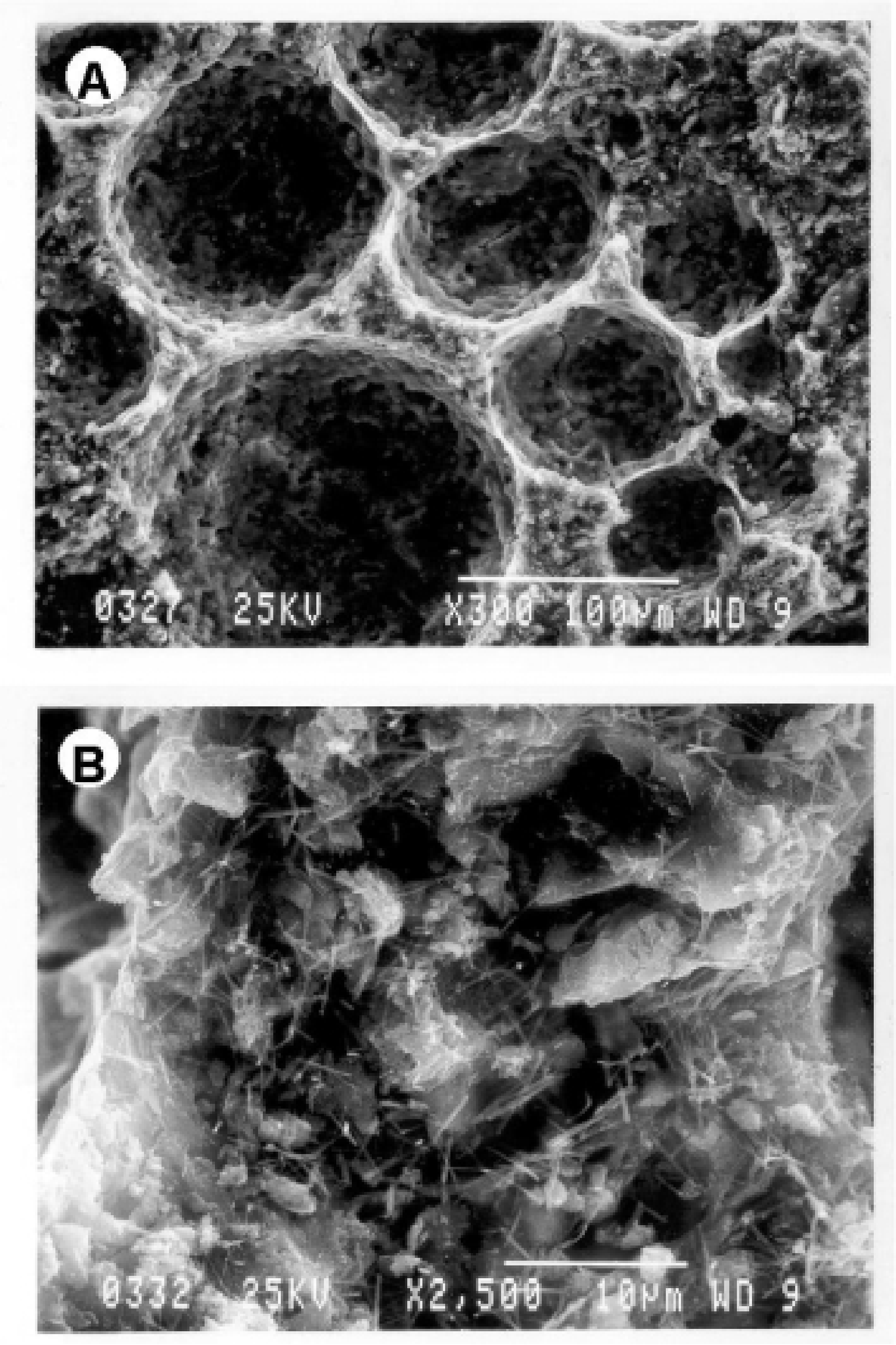


Figure 28. SEM micrographs of low strength specimen showing microstructure in regions of air void concentrations. A. Air void cluster on surface of quartzite aggregate (3663 psi). B. Microstructure of bubble wall between air voids in A. Bar scale is 100 µm in A and 10 µm in B.

Further examples of the variation in paste microstructure are given in the SEM micrographs in Figure 29. Figure 29A illustrates the relatively dense, fine-grained and nonporous microstructure typical of normal strength concrete. By contrast, Figure 29B, of low strength concrete, shows a porous microstructure consisting of coarse-grained plates, needles, and spongy aggregates that appears to have grown in an environment of open space. Porous paste microstructure of the interfacial zone low strength specimens included platy and needle-like crystals as well as spongy, arborescent C-S-H phases (Figure 30).

The presence of ettringite was confirmed on the basis of EDX analysis in the interfacial zone in both limestone and quartzite aggregate and cement paste (Figure 31). Distinctive $Ca(OH)_2$ plates up to about 50 μm in length were also observed in the interfacial zone (Figure 32).

The diameter of air voids in low strength specimens does not differ noticeably from those in normal strength specimens based on SEM observations of this study. The focus of observations was the transition zone between aggregate and cement paste. In the interfacial zone of both normal and low strength specimens, most entrained air had diameters between 20 and 150 μm (Figure 33). In both normal and low strength specimens, however, there were rare air voids up to 300-400 μm in diameter.

Discussion of SEM Results

SEM examination of the chemistry of the transition zone using EDX mapping and the phase composition of specimens using BSE imaging and EDX analysis did not yield clues regarding the low strength of the specimens. Similarly, SEM analysis of two types of cement powders using BSE and EDX did not point to significant compositional differences.

SEM examination during this study focused on air void distribution and paste microstructure in the interfacial zone between aggregate and cement paste. The correlation between low compressive strength and failure through the interfacial zone (Figure 22) indicates that bonding between paste and aggregate was inadequate and possibly a factor contributing to low strength.

The following conclusions are drawn based on the SEM study of the transition zone:

1. During sample preparation, low strength specimens (<4000 psi) failed primarily by debonding at the aggregate-paste interface, whereas in normal strength specimens aggregate-paste bonds were more likely to remain intact.
2. Debonded aggregate from low strength specimens typically showed high concentrations of entrained air on the aggregate surfaces (or the mold surface in the paste), whereas comparable concentrations were rare or absent on the surface of debonded aggregate from normal strength specimens.
3. Air voids on aggregate surfaces from low strength specimens were typically clustered or flocced, whereas comparable clusters were rare or absent in normal strength specimens.
4. The transition zone containing high air content is on the order of 100-400 μm in thickness;

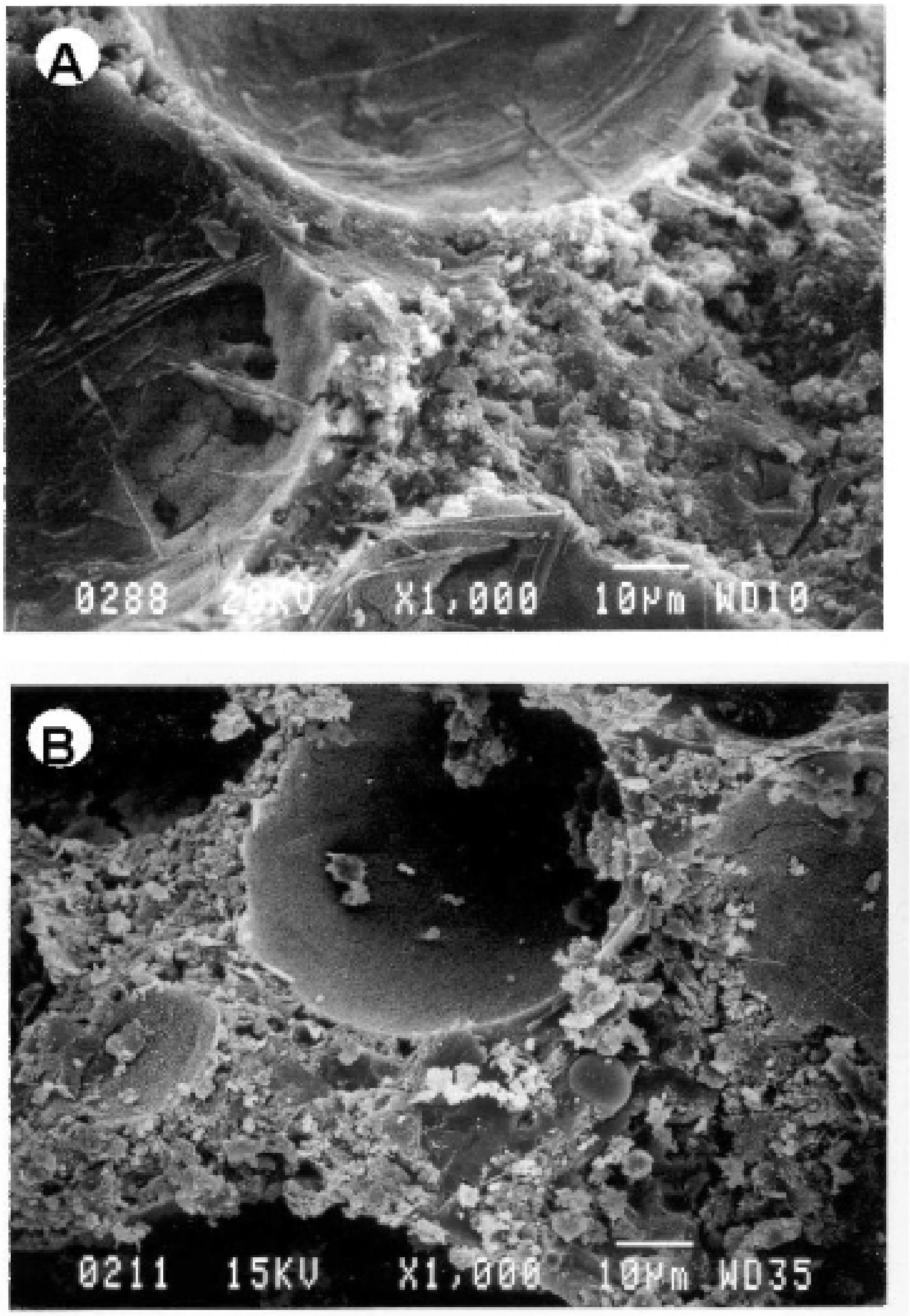


Figure 29. SEM micrographs of paste microstructure in interfacial zone. A. Relatively high strength specimen (4622 psi) with quartzite aggregate. B. Relatively low strength specimen (3910 psi) with limestone aggregate. Bar scale is 10 μm.

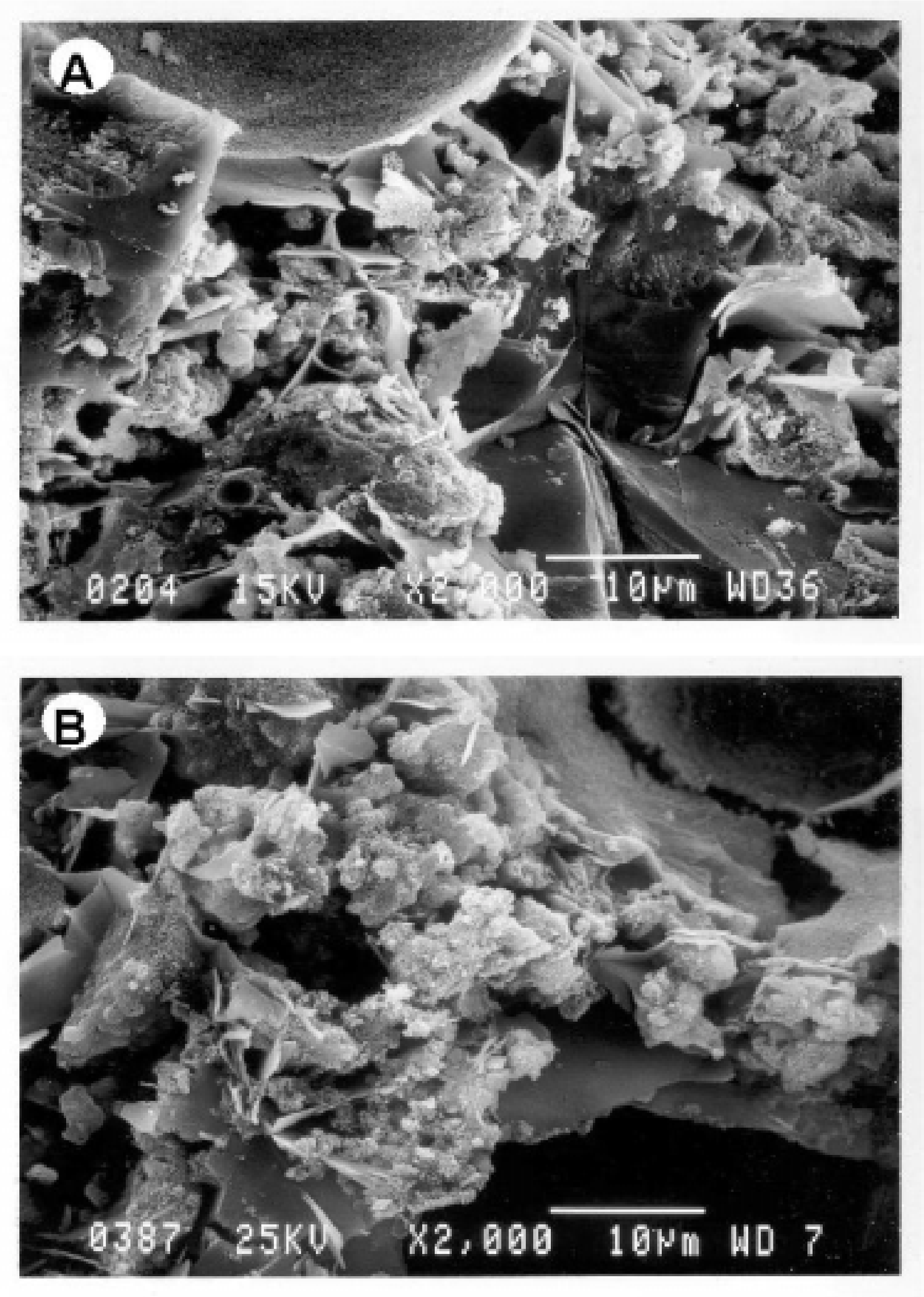


Figure 30. SEM micrographs of low strength specimens showing porous paste structure in interfacial zone. Phases include $Ca(OH)_2$ plates and spongy C-S-H. A. Limestone aggregate (3910 psi). B. Quartzite aggregate (3272 psi at 14 days). Bar scale is 10 m.

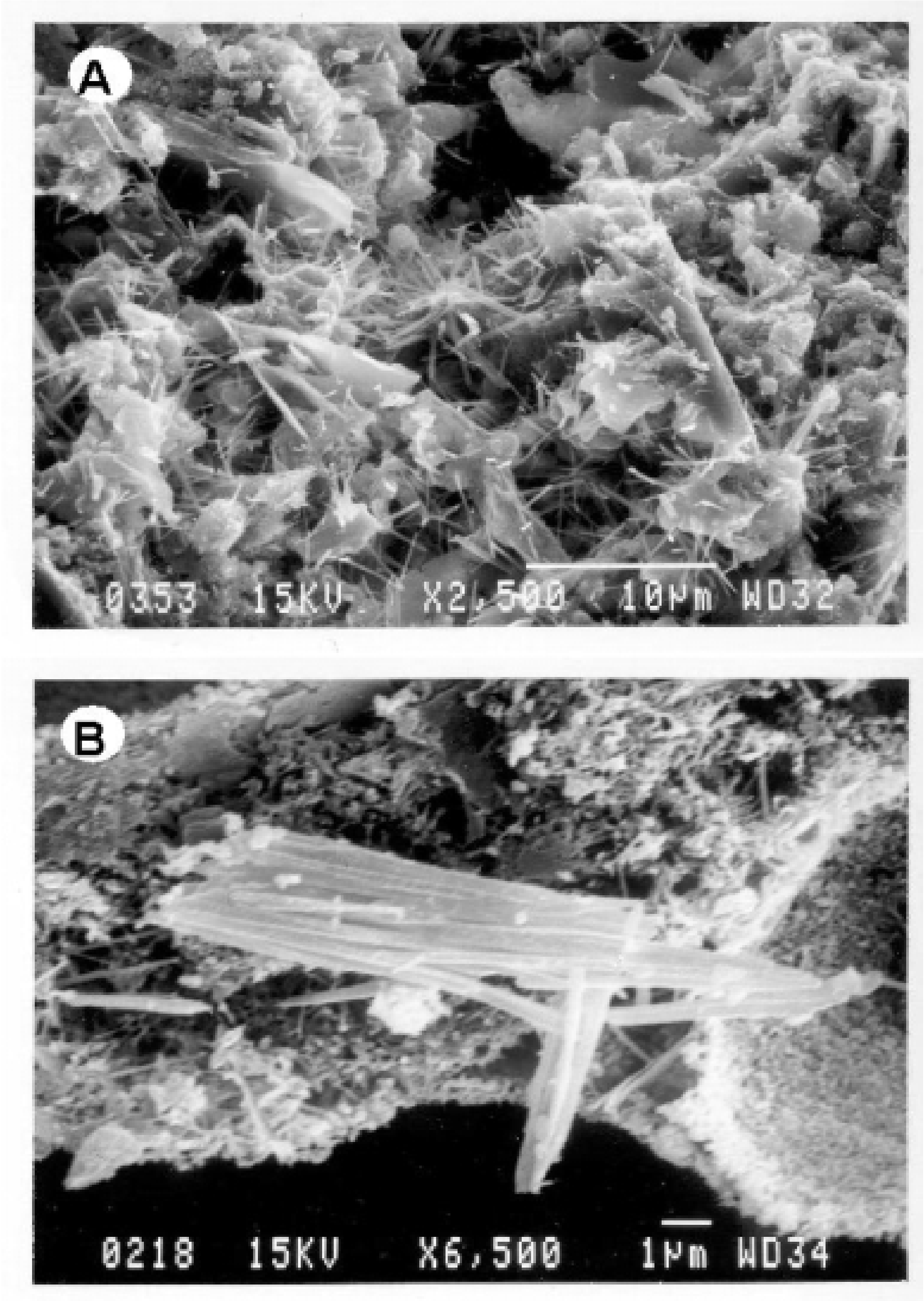


Figure 31. SEM micrographs of low strength specimens showing ettringite in interfacial zone. A. Limestone aggregate (3520 psi). B. Quartzite aggregate (3663 psi). Bar scale is 10 µm in A and 1 µm in B.

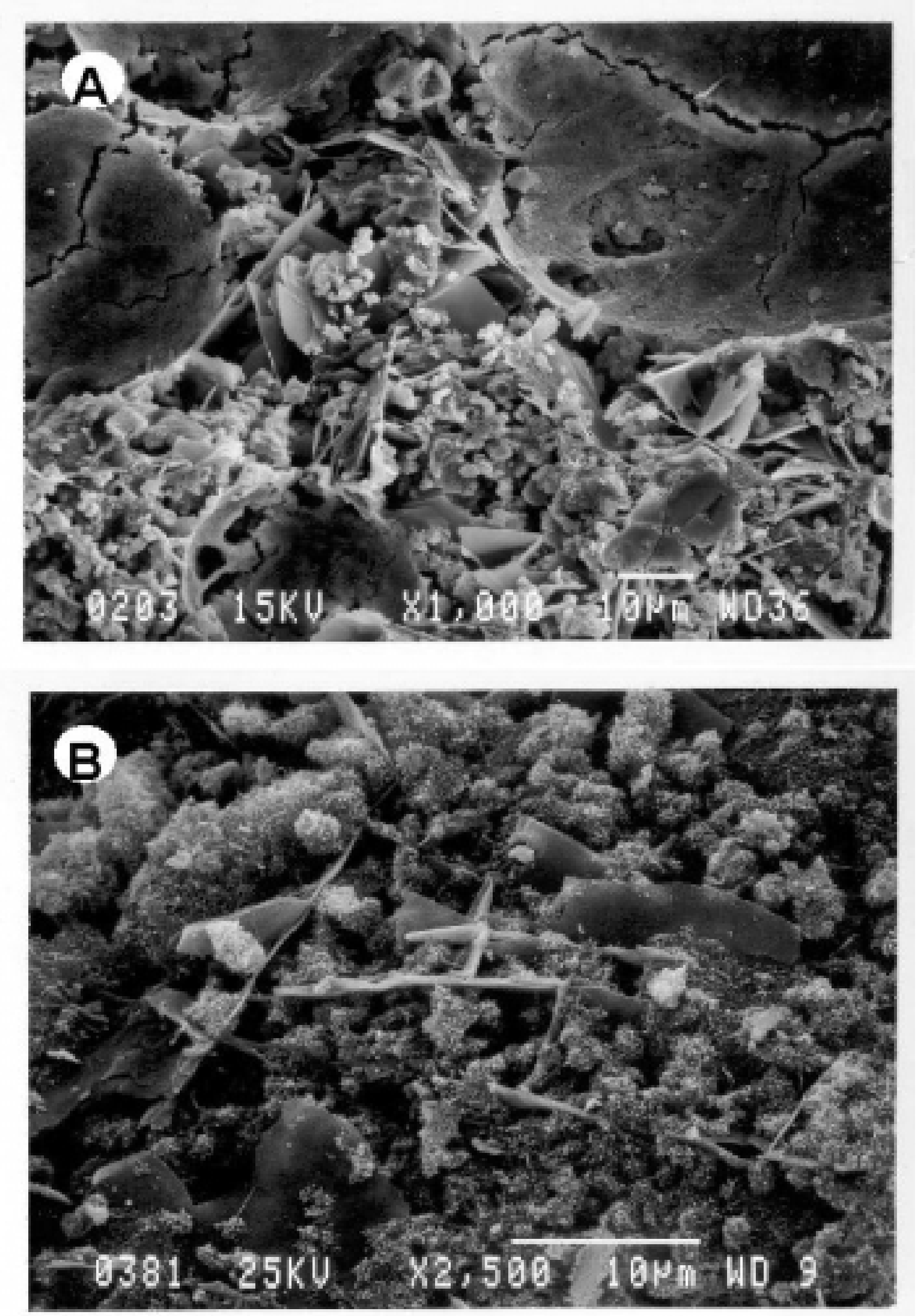


Figure 32. SEM micrographs of low strength specimens showing $Ca(OH)_2$ plates in interfacial zone. A. Limestone aggregate (3910 psi). B. Quartzite aggregate (3272 psi at 14 days). Bar scale is 10 m.

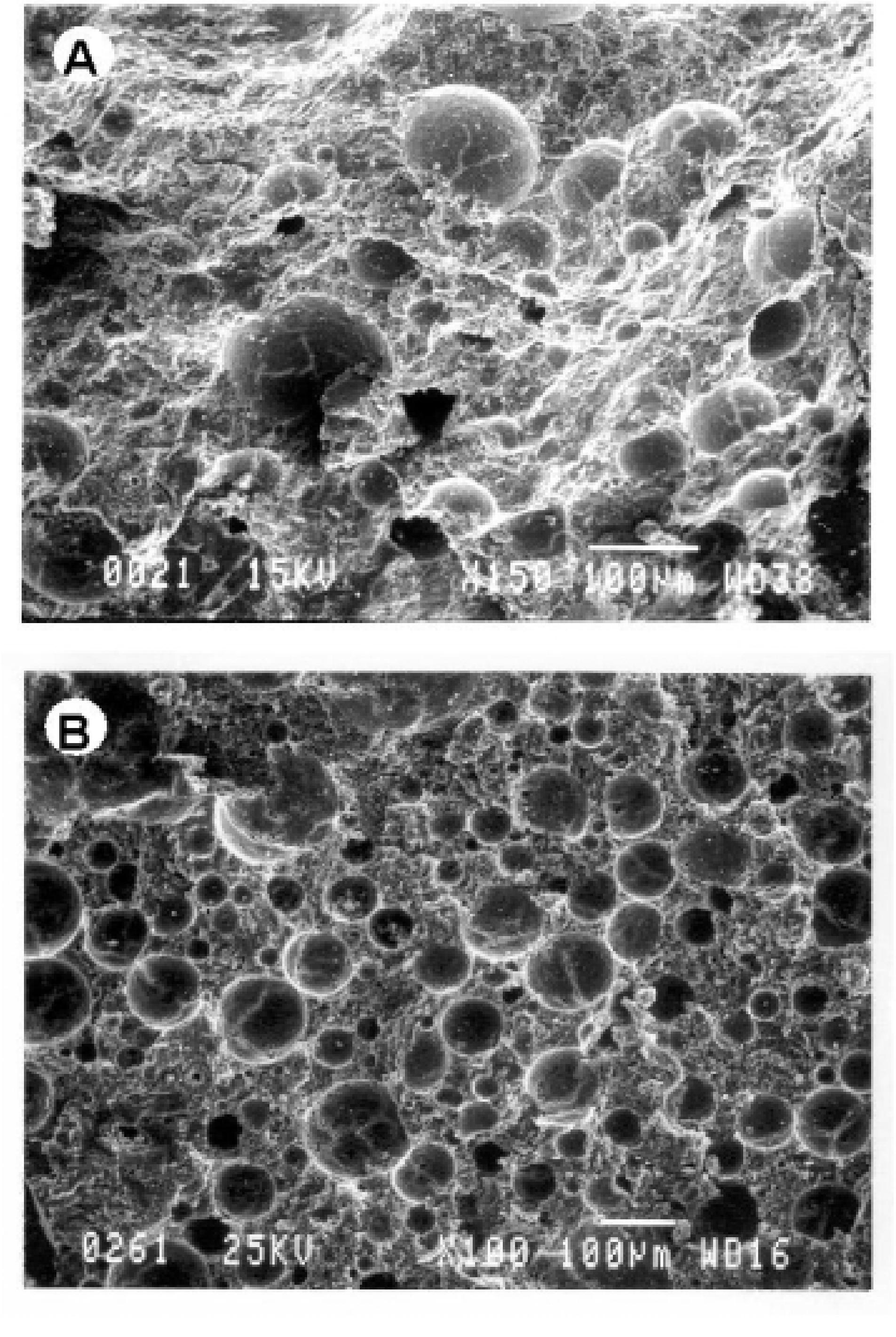


Figure 33. SEM micrographs showing air void sizes in normal and low strength specimens. A. Normal strength specimen (4485 psi) with quartzite aggregate. B. Low strength specimen (3660 psi) with limestone aggregate. Most air voids are between 20 and 150 μm in both specimens. Note: bar scale is 100 μm but micrographs are not at same magnification.

5. the zone typically contains a planar alignment of scattered or flocced air voids, which are rarely more than one bubble deep.
6. Debonding at the aggregate-paste interface occurs by failure through the centers of these air voids aligned in the transition zone; this appears to be the structurally weakest point in the concrete, especially in cases where air voids are clustered or flocced.
7. The microstructure in the transition zone of many low strength specimens is anomalously open and porous, consisting of needles (ettringite), plates ($Ca(OH)_2$), and spongy masses of C-S-H.

Petrographic Analyses

Purpose: Petrographic analyses were conducted to examine the air-void systems, microstructure, cracking phenomena and constituents of the concrete cores and materials used in this work. Petrography was performed to examine possible causes 1 (cement), 5 (high water-to-cement ratio), and 6 (high air content).

Results Cement Analysis:

Petrographic analysis of cement 1 and 2 was performed by Campbell Petrographic Services (Dodgeville WI). Cement 1 contained finer silicate particles. Also, in cement 1 alkali sulfate phases were found to be common, perhaps up to 1 % by weight. C3A was estimated at between 1 and 2 % in cement 1. This correlates well with the X-ray diffraction data which showed 1.0 weight % C3A for cement 1. For cement 2, more free lime was found, 0.35 % in cement 2 compared with 0.15 % in cement 1. Alkali sulfate was observed in cement 2 at an estimated percentage of 0.25 %. There were small differences in the average size of the alite and belite particles for the two cements. Cement 2 particles were 3-4 microns bigger on average. Finally there appeared to be more tightly packed belite nests in cement 1, although no statistical counting was performed. These belite nests can reduce the 28 day strength of concretes. The larger size of particles is expected to slightly increase the 28 day strength of the concrete by 2-3 MPa (300-400 psi).

Results Core Analysis:
State specifications require compressive strength and petrographic analysis testing of cores from projects with low compressive strength cylinder breaks. Petrographic analysis failed to identify the cause of low compressive strengthswhich occurred on almost 20 different construction projects. Further samples were taken for petrographic analysis as part of this research project. Cores from 4 field structural concrete projects were examined by petrographic analysis. Also, 9 cylinders from laboratory experiments were examined petrographically. These petrographic analyses were conducted by Campbell Petrographic Services, Inc. (Dodgeville, WI). For the laboratory cylinders, the water to cement ratio was between 0.38 and 0.42 for all cylinders, calcium hydroxide was found to be 4-6 % for all cylinders and the paste percentages ranged from 26.8 to 31.5 %. No evidence for air-void clustering around aggregate was observed with the possible exception of one cylinder. For the field specimens, two of the cores showed poor air-void systems one with only 2 % air (Core #1 [sic] also labeled Core #2, P0079(53)59 9/16/97,

PCEMS 4656 and the other Core #2 (P0079(53)59 6/27/97, PCEMS 4656 with marginal spacing factor and specific surface area. In addition Core #2 exhibited a remarkable amount of clustering, forming subhorizontal to irregular bands over and beneath the coarse aggregate, but also in the mortar fraction, giving the appearance of inadequate consolidation. The air system in this core is dominated by clusters of air voids, the clusters up to 30 mm long, some of which are connected with major and minor cracks. Compressive and flexural strengths would undoubtedly be seriously decreased, as well as durability. A third core (Core #1 CS6359(01)38 Jones PCEMS 393H) also exhibited significant clustering of air voids, a few clusters occurring adjacent to coarse aggregates. However, the non-clustered air voids were thought to be sufficient to provide an air void system capable of adequate freeze-thaw durability.

X-ray Computed Tomography

Purpose: As much of the data gathered for this project indicated a problem with the distribution of air within the concrete, a method was sought that could better examine the air distribution within concrete. One method that was tested showed very promising initial results. This was the use of X-ray computed tomography (X-ray CT). X-ray CT was conducted to examine an unlisted possible cause, uneven distribution of air within the concrete.

Method: X-ray CT is similar to a medical CAT scan except that much higher energy X-rays are used. These higher energies are necessary to penetrate the samples. In addition, X-ray CT can give a three dimensional (3D) reconstruction of the density differences within a sample.

Results: Figure 34 shows one 3D view of a portion of the core whose SEM image is shown in Figures 1 and 2. The air bubbles are clearly visible. The size of a volume element is equivalent to an air void diameter of ~50 μm. For this cylinder which was 1 cm in diameter and 1 cm in length, the percentage of air voids was estimated to be 3.3 %. This may be slightly low due to not counting voids whose diameter was less than approximately 30-40 μm or due to the sample having more aggregate than the concrete as a whole. Figure 35 shows a 2D slice of the X-ray CT image and it can be seen that the dark air voids are not evenly distributed within the paste and that there is some clustering of air voids in the vicinity of the aggregate.

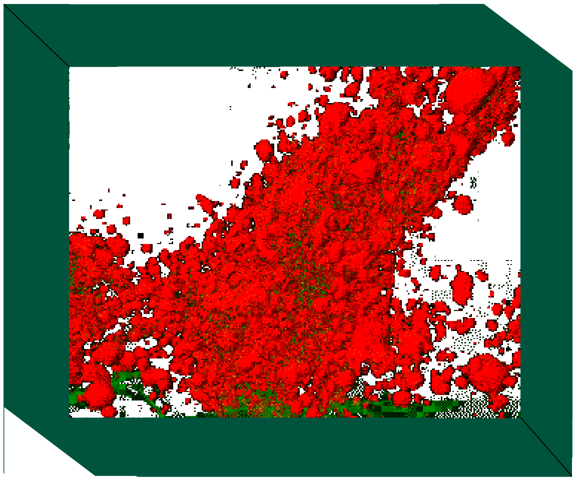


Figure 34. 3-dimensional depiction of air voids in concrete by X-ray CT. Air content in this image is approximately 3.3 %. Air voids are red, sample surface is green.

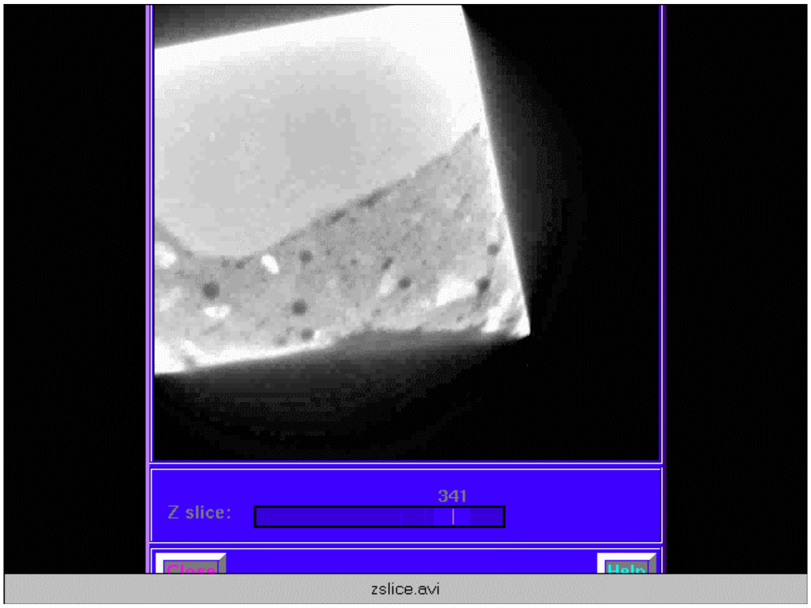


Figure 35. 2-dimensional slice of concrete sample by X-ray CT.

Cause of Low Compressive Strength Problem

From the results of the tests found in this report, the low compressive strength problem seems to be related to a combination of four factors. These factors are the type of air entraining admixture used, the temperature, the cement used and the presence of large amounts of air voids at the aggregate interface. While the data collected here do not unequivocally measure the effect of each of these factors, several interesting points have emerged. In controlled testing of two cements, the primary difference between these cements was that the cement that worked poorly (cement1) had significantly more alkali sulfates and percent soluble alkalis. There also seemed to be a difference in the hydration of some of the cement minerals. Second, several of the synthetic admixtures, which showed strength problems, also exhibited a greater tendency to adsorb to the aggregate surface. This adsorption causes the aggregate to be more hydrophobic. Third, the vinsol resin based admixtures kept considerably more water in their foams and drained much more slowly than did the synthetic admixtures. Furthermore, the air bubble walls are as much as twice as thick for the vinsol resin based admixtures. Finally, the paste formed in the low strength concretes has very low strength when compared to higher strength concretes.

The method by which low compressive strengths result is envisioned as follows:

1. As the concrete is mixed, air bubbles are formed within the mixture and some of these bubbles become attached to the aggregate surface. The longer mixing proceeds the more bubbles become attached. This is true for both vinsol resins and synthetic admixtures but the probability of attachment is greater for the synthetic admixtures.

2. The air bubbles clustered at the aggregate surface are similar to a foam. For the synthetic admixtures, the liquid drains quickly and very little water is left between bubbles. For vinsol resins the liquid drains much more slowly and much more water is present between the bubbles.

3. Any alkali sulfate present quickly dissolves into the pore solution. The sodium and potassium ions hinder the dissolution of calcium ions. Thus the water between the bubbles has more alkali and less calcium which hinders formation of the C-S-H gel. The low C_3A content of the cement results in slow hydration which also reduces available calcium immediately after mixing.

4. The relative lack of water and calcium between the bubbles at the aggregate surface leads to a very poor quality paste and a highly porous area adjacent the aggregate. The lack of water may explain the observation during the 1997 construction season that a smell characteristic of unhydrated cement paste occurred repeatedly throughout the 1997 construction season and was correlated with low strength concretes. The lack of water between the bubbles resulted in some of the cement paste remaining unhydrated.

5. The pores and air voids reduce the load transfer capability of the interface and the poor quality paste can carry only carry 1/3 to 1/6 of the load before breaking as can a good paste. If sufficient aggregates collect enough air bubbles the strength of the concrete is compromised. It appears that an increase from 40-50 % of aggregates to 75 % of aggregates failing in this fashion

can reduce the 28 day compressive strength from ~4500 psi to ~3500 psi.

6. The effect of temperature is not clear but in many mineral processing systems, particularly those using unsaturated carboxylate-based surfactants, the hydrophobicity of minerals that adsorb the surfactant significantly increases as the temperature increases. Also, the water drainage rate may increase due to the reduction of the viscosity of the water. Higher temperatures also act to stabilize foams and would explain the seasonality of the low compressive strength failures.

Summary

The original list of possible contributors to the low compressive strength problems which occurred during the 1997 construction season was:

1) cement
2) dirty rock
3) mix design too harsh
4) air entraining admixtures
5) high water-cement ratios
6) high air contents
7) temperature
8) concrete mixing time

The first two items examined with respect to cause were the obvious ones associated with low compressive strengths-high air contents and high water-cement ratios. A database comprising all A45 concrete cylinder test results was checked to determine how many failing tests could be attributed to air content > 8 % and slump > 4.5 “. Of 91 failing tests, only 8 had high air or slump. Complete project records from almost all 1997 projects with failing compressive strengths were also examined in detail on a project by project basis to see if there were any possible explanations arising from changes in concrete production during the course of the project without providing any potential explanations. In addition, petrographic examinations of numerous cores from low strength concretes throughout the state had estimated air contents and water-cement ratios well within specifications. Next, the possibility of dirty rock as a factor was investigated primarily by obtaining 11 different coarse and fine aggregate samples for laboratory concrete mixes from around the state. Standard gradations were run on these samples and none failed to meet the requirement for the maximum amount of combined material passing the #200 sieve (2.00 %) or the maximum deleterious substances (2.00%). Wiping the surfaces of the coarse aggregate revealed that all were coated with a film of rock dust from the crushing operations. ACI 221R-89 Guide for Use of Normal Weight Aggregates in Concrete states that ‘Clay coatings will normally interfere with bond, while nonadherent dust coatings increase the water demand as a consequence of the increase in fines.’ Ironically, the only coarse aggregate source with clay as an adulterent was a crushed limestone with friable shale pieces which had no failing compressive strength tests associated with it during the 1997 construction season.

The results of field data compilation, laboratory testing, petrographic and Scanning Electron Microscopy as well as information from other state DOT’s leads to one inescapable conclusion-the low compressive strengths experienced on structural concrete projects statewide during the 1997 construction season were directly related to the use of “synthetic” or non-vinsol resin air entraining admixtures. The evidence is fairly straightforward and physical and chemical test results provide a supporting framework.

The low compressive strengths which occurred in 1997 were not an isolated incident but represented a trend which was becoming noticeable during the latter half of the 1996 construction season. The most alarming aspect of these occurrences was the extremely low 28 day strength values obtained from concrete mixes specified by the state and used successfully for more than two decades. The overriding question with regard to the problem was “What has changed?”. The answer is cement, aggregate gradations, neoprene pads for compressive strength testing and air entraining admixtures.

The primary cement used in South Dakota is manufactured by Dacotah Cement in Rapid City. Dacotah had reformulated their cement composition to increase the C_3S content in 1996 with the goal of increasing 28 day compressive strengths and admixture compatibility. Could this new composition be responsible for the low strengths? The answer, based on several lines of reasoning, is no. Dacotah Cement provided a graphical summary of proprietary ASTM C109 compressive strength test results which showed a uniform product with an average 28 day compressive strength well in excess of 6000 psi. These results were confirmed by independent ASTM C109 testing done by SDDOT on project cement samples for 1996 and 1997. No tendency for lower than usual strengths was apparent. In addition, low compressive strengths occurred on projects where three other cement sources were used. These cements were all similar in composition to the Dacotah Type I-II Low Alkali specified.

Fine aggregate gradation has changed over time with a tendency toward lower fineness moduli apparent probably due to the removal of coarser sand fractions for use in chip seals. Discussions with industry indicated that the 60/40 coarse-to-fine aggregate ratio may be to high, yielding harsh mixes with poor dispersion. A series of concrete mixes of varying cement contents and aggregate ratios were tested to determine if this was the case. The results did not support the aggregate ratio as a significant factor in the low strength problem although they did justify widening the coarse-to-fine aggregate ratio range to 55-60/40-45 to improve workability. Another aspect of these additional tests was the striking reduction in compressive strengths when air contents exceeded 7.5 % with vinsol resin air entraining agent. This is illustrated in Figure 10 which clearly shows the marked affect of air content on strength above 7.5 %.

The final major change which occurred over the same time span as the low strengths was the shift in air entraining admixtures toward the “synthetic” air entraining agents. As early as 1995 SDDOT personnel were told by several members of the industry that vinsol resin air entraining agents would no longer be available as the cosmetic industry was purchasing the resin and driving the price beyond an economical range for use in concrete. This was the basis for a gradual shift toward the “synthetic” AEA’s. During 1995 and 1996 many of the air entraining agents used in concrete in South Dakota were purportedly mixed systems of vinsol resin and “rosins” because of the price situation. In 1997 almost every structural and paving concrete project employed the new “synthetic” AEA’s with the exception of low slump bridge deck overlays where vinsol resins were still extensively used. A check with Hercules Inc. Resins Division, Wilmington, Delaware, sole manufacturer of vinsol resin in the United States, during late 1997 revealed that the supply of vinsol resin was not a problem and its use in the cosmetic industry was not the source of the supply shortage. Hercules had shut down one of the two plants which manufactured vinsol resin around 1985 and were supplying the material from stockpiles and the other plant until 1992 when the sole source of vinsol resin was current production from the remaining plant. The price began to rise at this point but production was maintained at millions of pounds per year.

The primary focus of this research was directed towards the plausible explanation for the low compressive strengths being an interaction between the “synthetic” AEA’s and the cement resulting in a very poor quality bond interface between the cement paste and the aggregate. Cylinder and core failures of low strength specimens under compressive loading exhibited shear failure at the bond interface with little aggregate fracture and almost no cement paste retention on aggregate surfaces. Petrographic examination of low compressive strength cores failed to identify the source of the problem. Initial SEM work showed air void clustering at these interfaces and follow-up work showed the same phenomenon with a general increase in incidence as compressive strength dropped. The SEM also revealed extremely poor crystallite structure in the interfacial zone cement paste near these bubble clusters. Vinsol resin can also form bubble clusters but the composition of the cement paste adjacent to these clusters is not adversely affected.

Laboratory concrete testing indicated that there was a definite interaction between various air entraining admixtures and cement which could result in a significant reduction in compressive strength. A different cement shipment from the same source did not exhibit the same behavior which suggests that some difference in chemical or physical properties between the cements may be exacerbating the problem. The primary difference between the cements was found to be the available alkali sulfates, as both petrographic and chemical analysis indicated the poorly-performing cement had significantly higher soluble alkali sulfates. This is consistent with interaction effects which occur immediately upon water addition to the concrete as the alkali sulfates are freely water soluble.

Further laboratory testing of the chemical and physical properties of vinsol resin and other air entraining admixtures provides a mechanism for the development of air void clusters and poor quality cement paste at the aggregate-paste interface. The presence of void clusters alone does not constitute an explanation for low compressive strengths but when the frequency of these clusters reaches a critical threshold, strength will diminish dramatically. The presence of a uniform paste adjacent to aggregate surfaces is also critical for normal strength development. Vinsol resin exhibits marked differences from any other air entraining admixture tested and these are reflected in the superior performance achieved with vinsols. They are less hydrophobic, less sensitive to temperature, create more stable bubbles and drain water much more slowly than the “synthetic” AEA’s.

This research is not exhaustive enough to preclude alternate explanations for the low compressive strength problem in South Dakota. Field evidence, on the other hand, argues strongly in favor of air entraining agents contributing directly to the problem. In April, 1998, interim guidelines for concrete were initiated which restricted air entraining agents to vinsol resins and continued the use of water reducers as necessary. The 1999 construction season produced only three compressive strength tests lower than 4000 psi at 28 days for A45 concrete with a total of 15 tests below 4500 psi out of 703 total tests. Of these fifteen, one test was on frozen cylinders, five were on cylinders with air contents =8.0% and nine had low unit weights. Interestingly, one project which had a compressive strength test of 3820 psi also had a synthetic air entraining agent available at the plant when sampled and no vinsol resin on site. The 1999 construction season saw a reduction in failing compressive strength tests to an acceptable level of 2.14%, which compares favorably with the 8.77% failure rate from 1998 and the 14.9% rate for 1997. The overall average A45 compressive strength for 1999 is 5573 psi..

Conclusions

1. The extremely low compressive strengths experienced on A45 structural concrete during the 1997 construction season were the result of weak bonding at the aggregate paste interface associated with air void clusters and poorly formed cement paste matrix.

2. The use of water reducing admixtures reduced the incidence of low strength concretes but did not eliminate the problem.

3. The non-vinsol resin air entraining admixtures were the primary source of the strength problem due to an interaction with the low alkali cements used which promoted formation of air clusters and non-uniform cement paste at the aggregate interface which was exacerbated by the higher temperatures of summertime construction.

4. The chemical and physical properties of the “synthetic” air entraining admixtures are substantially different from vinsol resin as they are more hydrophobic, form thinner-walled air bubbles and do not entrain air as rapidly.

5. The foam test with cement added provides a rapid method for screening air entraining admixtures for performance as compared to vinsol resins.

6. Mixed vinsol resin-synthetic air entraining admixtures behave substantially the same as vinsol resin alone at vinsol contents of 50 % and greater.

7. Concrete mixes using vinsol resins for air entraining with air contents greater than 7.5 % are subject to a precipitous drop in strength.

8. The exclusive use of vinsol resin-based air entraining admixtures for structural and paving concrete has eliminated low compressive strength problems.

Recommendations

1. Continue the use of vinsol resin air entraining agents in all concrete.

2. Continue the use of water reducers as needed.

3. Maintain current cement contents for different classes of concrete mixes.

4. Restrict maximum air content in all concrete to 7.5 %.

5. Allow sand content in concrete up to 45% to improve dispersion and workability.

6. Allow the use of fly ash in structural concrete to improve dispersion, workability and reduce concrete permeability.

7. If market forces restrict the availability of vinsol resin, allow the use of resin-synthetic mixtures with a minimum vinsol resin content of 50 % and use the foam test to screen potential mixed AEA’s.

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Table A-1 Project Summary

Project	PCEMS	Aggregate	Air	Pour Type	StrengthTests	Water Reducer	28 Day (psi Avg)	Failing Cylinders	Comments	Failing Air and Slump Tests
BRO 8003(16)	0005S	Q	Davavair	Deck	2	Daracem 50	6370	0	FA used	2 slump
				Abutment		None	5205	1	backup 4710	1 low air
BRF 6227 (4)	015H	L	Airtite 60	Drilled Shaft	2	WRDA64	5820	0		0
				Deck, Etc	8	None	4716	2		0
BRO 8006(20)	022S	Q	Daravair	Box	8	None	4856	1		0
CS6231(01) 62	168P	Q	Daravair 1400	Deck	1	None	4930	0		0
CS8027(06) 27	025S	Q	Daravair 1400	Box	9	None	4891	2	3820	0
IM229-2(44)5	0548	Q	MBAE90	Bridge	39	None	5136	2	3820	0
				Bridge	15	Pozz344W Daracem 50	5378	0		0
P3806(22)145	166P	Q	Daravair 1400	Drilled Shaft	5	Daracem 50	4480	3	3570	0
				Bridge	10	None	4534	4		0
				Bridge	4		5715	1	1 bag/yd^3 cement	0
				Bridge	3	Daracem 50	6007	0		0
NH0212(74)87	2678	L	MBVR	Box	4	None	5440	0	Vinsol Resin	0
				Box	4	WRDA 60	6920	0		0
NH0014(109)422	3497	Q	Plastocrete l69	Paving	40	None	4748(868)	19	3150	3 air
				Paving	11	Plastocrete	4713(961)	4		0
NH0014(109)422	3497	Q	Darex 1000	Barrier	5	None	5130	1	4050	0

IM90-1(00)32	198P	L	MBVR Conc	Deck	1	None	6120	0	Vinsol Resin	0
				Low Slump	2	Polyheed 997	6295	0	Vinsol Resin	0
P2050(2)408	1369		Darex II	Bridge	19	None	5278	1	4100	0
BRF3037(2)8	1977	Q	Conchem Air	Bridge	15	Prokrete N3	5025	2	4140	0
BRO8064(6)	2617	Q	Darex II	Bridge	7	None	5724	0		0
BRO6355(8)	0215	Q	DarexII	Bridge		None	5124	1	Ashgrove cement	0
				Drilled Shaft	3	Daracem 50	5437	0	Ashgrove cement	0
BRO8014(9)	023S	Q	Daravair 1400	RCBC	3	None	4987	0		0
BRO8014(10)	024S	Q	Darex II	Bridge	9	None	4746	1	4430	0
BRO8042(22)	027S	Q	MBAE90	Deck	1	None	5180	0		0
BRO8064 (6)	2617	Q	Darex II	Bridge	7	None	5724	0		0
BRF3103(2)382	3788	Q	Pave-Air 90	RCBC`	7	None	5197	0		0
BRF6134(1)14	463W	Q	Darex II	Bridge	13	None	5625	0		0
P0079(53)59	4656	L	Conchem	Misc	38	None	5204 (573)	3	3820 (air 6.3 %)	
				Misc	15	Daracem 50	6157 (568)	0		
P3806(22)145	1666P	Q	Daravair 1400	Abutment	1	None	5800	0	7/1/97	2 high air
BRO8015(25)15	410H	G	Daravair 1400	RCBC	4	None Daracem 100	5622 (640) 5310 (427)	0	9/8-10/16	0
CS6231(01)62	168p	Q	Daravair 1400	RCBC	10	None	4895	2	5/23-6/10	0
BRO8006(20)	0225*	?	Daravair	RCBC	5	None	4856 (747)	1	7/24-8/5	0
CS6359(01)38	393H	L	Daravair 1400	Deck (pump)	2	Daracem 50	4225	2	4030 (6.2 % air)	0

				Bridge	2	None	5715	0		0
BFR3071(8)20	3152	L	Conchem AES	Drilled Shaft	5	Prokrete N3	5894 (807) + 10% cement	0	7/22-8/12	0
				Bridge	2	None	5730 (255)	0		0
				Bridge	19	Prokrete N3	5814 (807)	0	8/7-12/12	0
P0042(12)363	0773	Q	Daravair	Bridge Paving	69	None	5028	13	3640	0
P0045(12)192	1282	Q		Box	10	None	4070	9	3500	0
P0020(44)152	3154			Box	17	None	4767	2	3100	0
IM909(63)401	3467	Q	Polychem AE	Paving/ Bridge	20	None	6339	1	4160	1 high slump
IM908(73)362	3468	Q	Daravair	Bridge	9	Daracem 50	5460	1	4420	2 low air
NH0081(60)81	3509	Q	Conchem	Box	5	WRDA 19	4934	1	4100	
NH0012(00)107	3794		Conchem	Box	4	None	4957	1	3940	1 low air
P0044(00)78	3815	L	Conchem	Bridge	4	None	5586	1	4370	1 high air
P2050(2)408	1369	Q	Ad-Aire	Bridge	4	None	4906	1	1500 frozen cylinder	0
PPH0115(33)82	4449	Q		Paving	13	None	4440	7	3840	0
NH0014(00)418	4469	Q		Barrier Wall	7	Nome	4897	1	4280	0
BRO8049(9)	4612	Q		Box	6	None	4945	2	3980	0
P0079(53)59	4656	L	Daravair 1000	Bridges	47		5371	3	3820	0
IM905(86)251	4766		Darex II	Paving	26	WRDA 82	5130	2	4090	0
P0044(00)42	4832	L		Barrier	3		4463	1	3890	1 high air
P0044(00)82	4833	L		Barrier	5		3986	4	3200	0

Table A2 Summary of Laboratory Strength Tests

Type 1=ASTM C192 Type3=Water Reducer Mix N=non-heated
Type 2=3 minute mix Type 4=Non-Air Entrained Mix H=heated

	MIX$	TYPE	AIR	SLUMP	TEMP	UNIT	S7	S28	WC	AIR$
1	Coarse:	N1	5.9	4.00	73	143.8	3915	4380	0.459	ConchemAES
2	Hills Materials	N2	6.5	4.00	69	143.4	4133	5153	0.427	ConchemAES
3	Rapid City	N3	7.0	4.50	69	141.4	4185	4833	0.394	ConchemAES
4	Fine:	N4	3.3	4.25	69	146.8	4785	6117	0.446	NA
5	Hills Materials	H1	6.0	3.75	88	143.2	3370	4190	0.454	ConchemAES
6	Wasta	H2	5.5	4.25	92	144.8	3670	4423	0.441	ConchemAES
7		H3	5.2	4.25	88	145.0	4465	4753	0.421	ConchemAES
8		H4	4.0	4.50	88	146.8	3550	5253	0.434	NA
9	Coarse:	N1	5.8	4.00	74	145.0	3465	4850	0.416	Dar1400
10	Spencer	N2	5.4	3.75	70	144.6	4055	4400	0.416	Dar1400
11	Quarries	N3	6.4	4.00	69	143.8	3990	5360	0.403	Dar1400
12	Fine:	N4	2.4	4.00	69	149.2	4620	6367	0.442	NA
13	Opperman	H1	5.9	3.50	92	144.2	3575	4227	0.435	Dar1400
14	Sand	H2	4.8	3.50	94	145.4	3720	4587	0.428	Dar1400
15		H3	4.8	4.00	89	146.0	4440	5387	0.419	Dar1400
16		H4	2.0	2.75	90	149.4	4510	6210	0.447	NA
17	Coarse:	N1	7.3	4.50	70	142.8	3200	3914	0.405	Dar1400
18	Hills Materials	N2	6.1	4.00	70	144.6	3685	4845	0.392	Dar1400
19	Hot Springs	N3	5.9	4.00	70	145.0	3980	5358	0.373	Dar1400
20	Fine:	N4	2.8	4.50	70	149.9	4515	6289	0.405	NA
21	Hills Materials	H1	5.8	4.00	92	145.4	3210	4303	0.429	Dar1400
22	Opperman	H2	6.2	3.75	92	145.0	3770	4486	0.416	Dar1400
23	Sand	H3	5.2	3.75	95	146.6	3945	5117	0.410	Dar1400
24		H4	3.4	4.25	90	148.4	4330	5800	0.429	NA

25	Coarse:	N1	5.8	4.00	66	143.4	4085	5140	0.451	MBAE90
26	Concrete Mat.	N2	6.2	4.00	68	142.8	4100	5027	0.425	MBAE90
27	Sioux Falls	N3	6.8	4.00	68	142.6	4390	5397	0.399	MBAE90
28	Fine:	N4	2.8	3.75	68	147.8	5045	6547	0.444	NA
29	Concrete	H1	6.5	3.75	91	141.8	3300	4393	0.451	MBAE90
30	Materials	H2	5.3	3.63	93	143.8	3710	4390	0.445	MBAE90
31		H3	5.8	4.25	89	143.4	3800	4830	0.439	MBAE90
32		H4	2.8	3.75	90	147.0	4245	5980	0.464	NA
33	Coarse:	N1	5.7	4.00	68	144.6	3805	4707	0.441	Darex2
34	Concrete Mat.	N2	6.4	4.25	68	142.8	3945	5327	0.421	Darex2
35	Sioux Falls	N3	5.6	4.00	68	144.8	4340	5640	0.408	Darex2
36	Fine:	N4	3.2	4.00	69	148.2	4565	6760	0.434	NA
37		H1	6.0	4.00	94	143.2	3245	4043	0.484	Darex2
38		H2	6.4	4.25	92	142.8	3170	4670	0.451	Darex2
39		H3	6.6	4.50	90	142.4	3460	4767	0.432	Darex2
40		H4	3.2	4.00	88	147.0	4255	5740	0.477	NA
41	Coarse:	N1	7.1	4.00	70	142.8	3765	4803	0.414	MBVR
42	Concrete Mat.	N2	7.1	3.75	68	142.2	3965	4877	0.401	MBVR
43	Sioux Falls	N3	6.3	3.75	69	144.6	4640	5790	0.395	MBVR
44	Fine:	N4	2.8	3.50	69	148.6	5085	7207	0.421	NA
45		H1	6.3	4.25	89	143.0	3715	4507	0.458	MBVR
46		H2	5.2	4.00	94	144.6	3785	4890	0.445	MBVR
47		H3	6.5	4.25	94	143.0	3970	5507	0.432	MBVR
48		H4	2.6	4.00	91	147.6	4465	5580	0.471	NA
49	Coarse:	N1	7.1	4.75	70	141.6	3900	4833	0.422	Dar1000
50	Concrete Mat.	N2	5.3	3.75	70	144.8	4360	5537	0.397	Dar1000
51	Sioux Falls	N3	5.6	3.75	70	144.6	4640	5707	0.384	Dar1000
52	Fine:	N4	2.0	3.00	70	148.6	4855	6640	0.442	NA
53		H1	6.1	3.50	90	142.2	3300	4243	0.479	Dar1000
54		H2	6.4	4.00	92	140.8	3630	4800	0.486	Dar1000
55		H3	6.4	4.00	90	141.8	3650	4473	0.479	Dar1000
56		H4	2.7	3.00	94	147.4	4395	5823	0.486	NA

57	Coarse:	N1	5.9	4.00	68	146.8	3775	4530	0.410	ConchemAES
58	Concrete Mat.	N2	7.2	4.50	68	143.8	3900	5253	0.404	ConchemAES
59	Summit	N3	6.5	4.00	70	145.4	4560	5297	0.371	ConchemAES
60	Fine:	N4	2.8	4.00	68	150.3	5455	7620	0.416	NA
61		H1	5.6	4.25	97	146.4	3110	3945	0.443	ConchemAES
62		H2	6.0	4.00	99	144.8	3360	4985	0.423	ConchemAES
63		H3	5.8	4.25	98	145.4	4055	4677	0.423	ConchemAES
64		H4	3.0	4.50	96	148.8	4580	5587	0.456	NA
65	Coarse:	N1	7.2	4.00	68	141.6	3530	4610	0.400	Dar1400
66	L.G.Everist	N2	7.0	4.00	70	142.2	4085	5000	0.400	Dar1400
67	Dell Rapids	N3	7.4	4.00	70	141.8	4255	5623	0.367	Dar1400
68	Fine:	N4	3.2	4.00	69	147.8	4980	7113	0.406	NA
69	Hilde Sand	H1	7.5	4.00	95	140.2	3260	4123	0.444	Dar1400
70		H2	7.0	4.00	96	141.0	3460	4210	0.424	Dar1400
71		H3	7.2	4.00	98	141.0	3625	4953	0.412	Dar1400
72		H4	3.3	3.80	96	146.2	4530	6267	0.450	NA
73	Coarse:	N1	7.0	4.25	69	142.2	3920	4603	0.423	NVX
74	Concrete Mat.	N2	7.1	4.25	68	142.2	3775	5227	0.410	NVX
75	Sioux Falls	N3	6.4	4.00	70	143.2	4345	5357	0.404	NVX
76	Fine:	N4	3.0	3.75	70	147.8	5230	6687	0.436	NA
77		H1	6.9	4.25	92	141.6	2880	4470	0.458	NVX
78		H2	6.2	4.00	94	142.8	3330	4317	0.458	NVX
79		H3	6.2	4.00	90	142.6	4335	4837	0.451	NVX
80		H4	3.1	4.00	91	147.6	4595	6107	0.464	NA
81	Coarse:	N1	5.8	4.00	68	143.8	3900	5163	0.455	MBAE90
82	Myrl & Roy	N2	5.8	3.75	69	143.8	4075	5350	0.442	MBAE90
83	Nelson	N3	5.6	4.00	69	144.8	4540	5147	0.429	MBAE90
84	Fine:	N4	2.6	3.75	70	148.2	5140	6920	0.455	MBAE90
85	Higman Sand	H1	5.4	4.25	90	143.2	3530	4390	0.492	MBAE90
86		H2	5.5	4.25	92	143.4	3655	5067	0.459	MBAE90
87		H3	5.5	4.25	88	144.0	4365	5793	0.440	MBAE90
88		H4	2.6	4.30	88	147.4	4680	6150	0.485	MBAE90

89		N1	5.4	4.00	70	144.0	3950	4967	0.460	ConchemAES
90		N2	5.6	3.50	70	144.0	3945	5707	0.454	ConchemAES
91		N3	5.8	4.00	70	144.0	4270	5807	0.428	ConchemAES
92		N4	2.4	3.50	70	148.2	4720	6507	0.473	NA
93		N1	5.7	4.00	68	143.8	3905	5120	0.460	Dar1000
94		N2	5.2	4.00	69	144.4	4025	5080	0.454	Dar1000
95		N3	5.7	4.00	69	143.8	4340	5147	0.441	Dar1000
96		N1	7.0	4.25	67	141.5	3645	5300	0.412	MBVR
97		N2	6.2	3.75	67	143.6	3955	5690	0.412	MBVR
98		N3	6.0	4.00	67	143.8	4580	5547	0.399	MBVR
99		N4	2.0	4.00	67	149.9	4730	6703	0.464	NA
100		N1	5.4	4.00	66	145.0	3915	5213	0.451	Darex2
101		N2	5.6	4.00	66	144.0	3840	5500	0.438	Darex2
102		N3	5.6	4.25	67	144.4	4500	5700	0.412	Darex2
103		N1	6.6	4.25	68	142.2	3715	5077	0.438	Dar1400
104		N2	5.7	4.00	67	144.2	4290	5720	0.432	Dar1400
105		N3	6.0	4.00	68	144.0	4450	5407	0.412	Dar1400
106		N4	1.8	4.25	69	149.9	5085	6443	0.471	NA
107		N1	5.7	4.00	68	144.6	4360	5240	0.432	NVX
108		N2	5.3	3.75	68	145.2	4705	5777	0.425	NVX
109		N3	5.9	4.00	68	143.6	4615	5410	0.419	NVX